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WORKS ON HEAT-RESISTING MATERIALS

- USSR -

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# FOREWORD

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# WORKS ON HEAT-RESISTING MATERIALS

## - USSR -

Following is a translation of "Works of the Seminar on Heat-Resisting Materials 13-17 June 1958" published in the Russian-language periodical Byulleten' Institut metallokeramiki i spetsial'nikh splavov (Bulletin. Institute of Metal Ceramics and Special Alloys), No 5, Academy of Sciences, Ukrainian SSR, Kiev, 1960, pages 1-65.

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# FOREWORD

This collection of works is dedicated to the physical properties and the technology of preparation of refractory metals and their metalloid borides, carbides, nitrates and silicides.

It reports the results of investigations on absorption spectra and emission spectra of columbium and chromium compounds, the results of research into the processes of joint co-diffusion of two elements into metals, the data on the phenomenological study of the physical properties of the metalloid phases.

The basic principles for production of powders and articles from rare metals and refractory compounds are examined for the various fields of contemporary engineering.

The collection includes a number of reports which illuminate individual problems of the powder metallurgy of ordinary metals and alloys.

It is intended for engineers, scientists, students of polytechnical schools specializing in refractory metals and their compounds, in powder metallurgy, electronics, mechanical engineering and in the metallurgical science.

## PREFACE

Recently, more and more attention is being paid to refractory metals and heat-stable compounds in connection with their use in the manufacture of heat-resisting alloys, of special fire-proof hard alloys for metal working, of corrosion-resistant parts for chemical apparatuses as well as with their use in electronics, electric engineering, automation, and so on.

In the USSR, the conditions of obtaining the properties and applying these groups of metals and compounds were successfully investigated in many scientific research organizations, engineering bureaus, factory and school laboratories.

At the Seminar, conducted in Kiev on 13-17 June 1958, the results of a rather large bulk of work were expounded. The works were made in the Institute of Metal Ceramics and Special Alloys of the Academy of Sciences USSR, the Government Institute of Applied Chemistry (Leningrad), the Kharkov Polytechnical Institute, the Institute of Metals Physics, the Sverdlovsk Government University, the All-Union Institute of Aviation Material, the Central Scientific Research Institute of Ferrous Metallurgy, the All-Union Scientific Research Institute of Abrasives and Polishing, the Institute of Metallurgy of the Academy of Sciences USSR, the All-Union Scientific Research Institute of Fuel Recovery, the Scientific Research Institute of the Government Committee of Radio Engineering and Electronics, the Moskva Combine of Hard Alloys, the Gor'skiy Polytechnical Institute, the Moskva Electric Lamp Factory.

The editorial board was unanimous in considering it proper to publish in the present collection that part of the Seminar's material which pertains to the physical properties and crystal structure of the electronic arrangement of refractory compounds, since this part is interesting in itself, and includes a few theoretical questions of major importance.

# PHYSICAL PROPERTIES OF METALLOID COMPOUNDS

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AN USSR

The metalloid compounds include borides, carbides, nitrides and silicides of the transition metals (with closed electronic d- and f-levels).

The criteria of metalloid compounds are:

1) high degree of hardness reaching $3000$ kg/mm$^2$;

2) metallic shine and in the majority, metallic conductivity, at least at normal temperature;

3) high degree of thermal stability; as a rule, the melting or dissociation temperatures of those compounds are very high (up to $3500^\circ C$), and frequently above the melting temperatures of the most refractory metals and oxides;

4) brittleness and absence of plastic deformation at a temperature in the order of $0.85 - 0.95$ $T_{melt}$.

According to structure, the metalloid compounds can be divided into two kinds.

The first group includes the intrusion structures with closely packed metal atoms, i.e., the carbides and nitrides of the transition metals subjected to the law of Hägg:

$$r_x : r_{Me} \leqslant 0.59$$

where $r_x$ and $r_{Me}$ are the corresponding atomic radii of the metalloid and the metallic components.

In these compounds, the metalloid atoms are located in the interstices of the cubic or hexagonal close-pack of metal atoms, and they do not form bonds with each other. The bonds between the atoms of metal and metalloid bear a directional character which conditions high-grade hardness and brittleness of the compounds, and they have an octahedral configuration to which the hybridization of the bonding $d_2sp_3$ orbitals correspond [1]. Here, the d-electrons of the metal participate in the creation of the bond. This causes a decrease in magnetic susceptibility and a change in electric conductivity of the metals at the formation of metalloid compounds [2]. The maximum electric density (electron density) in the bond directions is here somewhat dislocated sideward to the metal atoms, owing to the incomplete structure of their d-shell and, consequently, to an incomplete shielding of the nuclear charge by the electrons of this shell [3,4].

The degree of dislocation of the electron cloud depends also

upon the strength of the metalloid electrons bond, i.e., to a first
approximation upon its ionizing potential, being diminished with the
increase of the latter. Since the ionisation potential of nitrogen is
higher than that of carbon, the dislocation of the electron cloud to
the metallic atoms is less in the Me - N bonds than in the Me - C
bonds. It is possible that, owing to its considerable electronegat-
ivity, which brings the nitrides close to the oxides, in the first
case the electron cloud is even dislocated toward the nitrogen.

On Fig.1 we indicated the emission spectra of the K-series
of titanium in $TiO_2$, $TiN$, $TiC$, $TiH_2$ and $Ti$ [5].
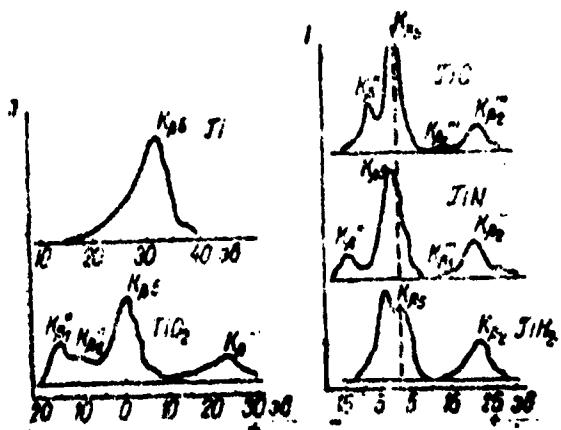


Fig.1. Emission spectra of the K-series of titanium
in $TiO_2$ and metalloid compounds.

(Abscissa: e7 = electron volts)

It can be seen that to the extent of the electronegativity and the ionizing potential of the metalloid, the long-wave constituent of the $K_{\beta_5}$-line is gradually strengthened with the latter, and it disappears in titanium hydride and metallic titanium, which probably is related to the gradual translation of the density maximum of electron cloud in the above quoted series of compounds to the metal, and also related to an increase in the density of the occupied states in the d-band of the metal, but the latter reduces the probability of patternless transitions. In the Me - X bonds, not all electrons of the two components are apparently occupied, which conditions the presence of free electric-current carriers, and the metallic conductivity of the intrusion phases.

The second type of metalloid compounds includes compounds with more complicated structure in which, parallel with the Me - X bonds, there are bonds between the metalloid atoms themselves. The possibility of the formation of such structures requires a mutual overlap of the bonding orbits of metalloid atoms, and it depends upon the relative sizes of the metal and metalloid atoms and upon the ease of excitation of the metalloid valency states.

The tendency toward the formation of complicated structures increases in this order: -- nitrides, carbides, borides, and silicides.

The carbides of complex structures are formed in case of

$r_x : r_{Me} > 0.59$  (chromium, manganese, elements of the iron triad).

The borides and silicides do not form simple intrusion structures at any value of $r_x : r_{Me}$. In these phases, to the extent of the metalloid content, the ground of the metalloid bonds is intensified, and single and double chains, two-dimensional grids, and three-dimensional structural frames appear in the lattice, formed by metalloid bonds with one another, which can be seen on Fig.2.
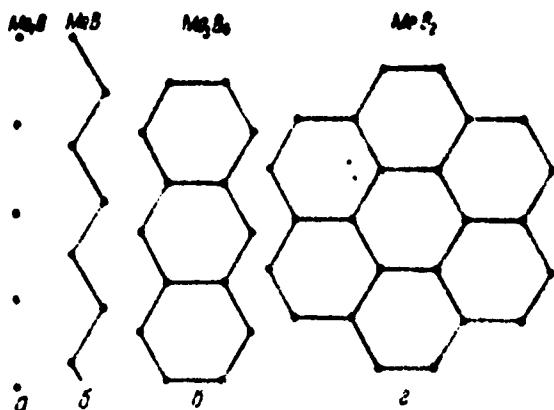


Fig.2. Diagram of the mutual bonds of boron with borides
of different composition.
(Letters at bottom: a,b,v,g...indicating a,b,c,d)

In the majority of cases, the distance X - X is close to the doubled common covalent radius of the metalloid atoms. Apparently, the Me - X bonds in all metalloid compounds are close by nature, which results in a qualitative similarity of their physical properties.

## Electrophysical Properties

The electronic structure of the metalloid compounds is the most clearly reflected in their electrophysical properties. G.V.Samsonov [6] observed that the electric resistance of the transition metals regularly increases with the increase of the acceptor capacity of the metal atoms (Fig.3). The latter can be evaluated to a first approximation by the criterion

$$\xi = 1/Nn$$

where N...is the main quantum number of the partially filled d-shell; n...is the number of d-electrons. The significance of magnitude $\xi$ (Greek x) is therein that the small N and n are, i.e., the larger $\xi$ becomes, the less the shielding is of the nuclear charge of the metal atom, and the more the atomic core is able to act as an acceptor of supplementary electrons /6/.
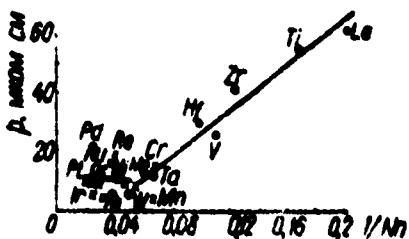


Fig.3. Relation of electric resistance of transition metals to their acceptor capacity($\xi$ ).
(On ordinata: r micro-ohm cm).

Increase in the acceptor capacity leads to supplementary elec-
tron scattering at the lattice points occupied by the transition met-
al atoms, and consequently to an increase in electric resistance. Com-
parison of the value of electric resistance  of the metalloid compounds
with the magnitude $\xi$  of the metals shows (Fig.4)  that the resistan-
ces of borides,carbides and nitrides regularly decrease with the in-
crease of the metal's $\xi$ .
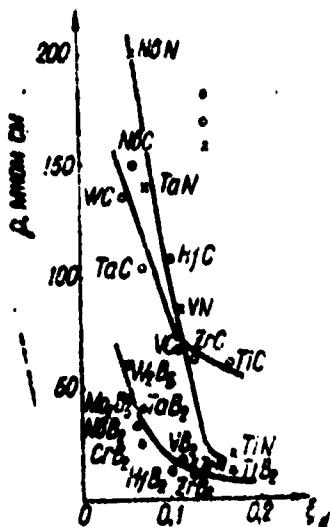


Fig.4.Relation of electric resistance of metalloid com-
pounds to the acceptor capacity($\xi$ ) of the metal
components:   ...borides; o...carbide; x...nitride.
(On ordinata: r micro-ohm cm)

This tendency is also observed for silicides,but it is less clearly
expressed. The cause of such a relationship is given by the follow-
ing. The increase in the acceptor capacity of metal atoms leads to

greater dislocation of the electron cloud in the Me - X bond direc-
tions toward the metal atom cores, which provokes a statistical de-
crease in the electron defect of their d-shell; consequently,its ac-
ceptor capacity and the scattering effect upon the conductivity elec-
trons decreases. The la. er in its turn leads to a reduction in elec-
tric resistance. The strength of interatomic bonding in the metalloid
compounds also happens to increase,as it will be indicated below. Con-
sequently,the effective cross-section of the phonons(lattice-vibra-
tion quanta) is reduced which seem to be also a source of the scat-
tering conductivity electrons. Due to this, with the growth of $\xi$, a
reduction in the electric resistance of metalloid compounds occurs
sharply.

For the hexaborides of fd- transitional metals with a $CaB_6$
type of structure, the growth in electric resistance was found to
run parallel with the enlargement of the atomic number of the metal-
lic component in the series $LaB_6 - CeB_6 - ...SmB_6$, which is related
to the reduction in effective concentration of the current's car-
riers( the free electrons),as a result of the elevation of the stab-
ility of the (4f)-state in this series and the difficulties of the
$f \to d$ transition [28,29].

Jointly with N.V.Kolomoits, G.V.Samsonov, and S.A.Semenko-
vich [7],we have investigated the thermal relation of electric re-
sistance of a number of metalloid compounds(Fig.5 - 8). The draw-

ings make it clear that for borides and carbides, the metallic con-
ductivity corresponds at all the examined temperature intervals, and
their resistance linearly increases with the temperature, which points
to an independence of the number of the current's carriers from the
temperature [8] and to a sufficiently full overlapping of the band of
valency electrons with the band of conductivity.
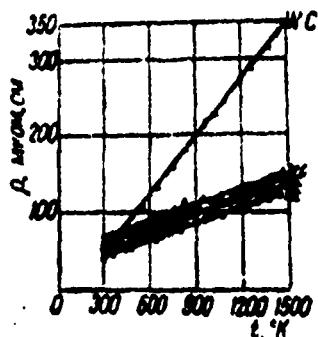


Fig.5.Temperature relation of
electric resistance of carbides.
(Ordinate: r micro-ohm cm).
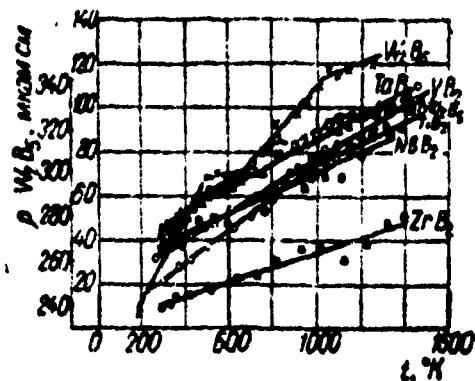
Fig.6.Temperature relation of
resistance in borides.
(Ordinate: r $W_2B_5$ microohm
cm).

Silicides and nitrides only show similar character of conductivity
at definite temperatures above which the dependence of their resist-
ance upon temperature diminishes, which can be related only to a
change in the mechanism of conductivity,since,at the examined tem-
perature range [9], no phasic transformations are observed for these
substances.
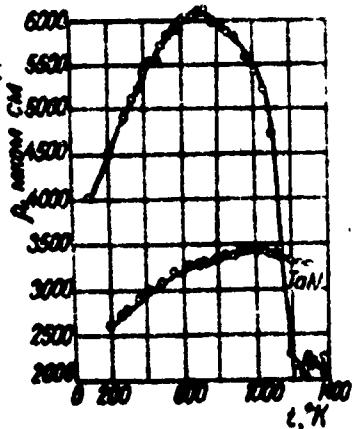
Fig.7.Temperature relation of
electric resistance of ni-
trides.
   (Ordinata: r microohm cm)
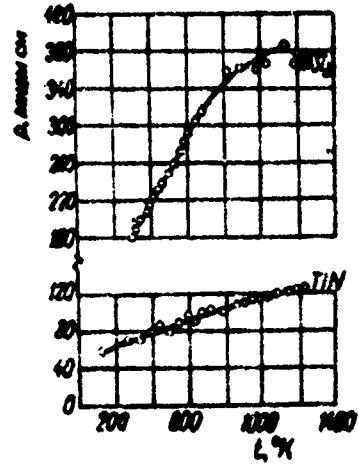
Fig.8.Temperature relation of
electric resistance of sili-
cides.
   (Ordinata: r microohm cm).

The reduction in resistance with the temperature growth is
related to a noticeable increase in the number of the current's car-
riers under the influence of warming-up, which is characteristic for
semiconductors [8]. The cause of change in the conductivity mechan-
ism in case of the examined silicides and nitrides* is apparently
found in a slight overlapping of the energy bands of the valency and
conductivity electrons,which at increased temperature causes the ap-
pearance of energy gaps between them,as a result of the increase
of interlaminar distances in the crystals. An analogous relation of
resistance to temperature was detected by L.N.Gusev and V.I.Ovechkin
for chromium disilicide [10].

*( [NOTE]: For titanium nitride, a deviation of the thermal relation of resistance from linearity was only detected. Apparently, the temperature obtained by us is not enough to cause a divergence of the valency and conductivity zones .)

In this manner, the borides and carbides of transition metals must belong to metal-type substances with substantial overlapping of the bands of the valency and conductivity electrons, while the ni - trides and silicides apparently belong to semimetals with a slight overlap of these bands.

The thermoelectromotive force arising in the metalloid compounds is not large, reaching the order of a few dozen microvolts by grade, i.e., it has the same order as also in case of metals [11,12]. Some silicides (CrSi$_2$ [10], MnSi and FeSi$_2$ [13,14]) are excluded. Their thermoelectromotive force has the order of $10^2$ micro-V/$^\circ$C, which emphasizes their intermediate position between metals and semi-conductors. With the elevation of temperature, the thermoelectromotive force of borides, nitrides, and silicides is increased (Fig.9 - 10), which points to the vacancy character of their conductivity ($+d\alpha/dT$), and for the carbides it decreases, which corresponds with the electron-type conductivity ($-d\alpha/dT$) [7]. Here the $\alpha$ designates the thermoelectromotive force for 1$^\circ$K.

Together with Samsonov and Kudintsev, we investigated the thermoemission parameters of the borides and transition metals [15]. It was shown that the work function of electrons from d-transition

- 13 -
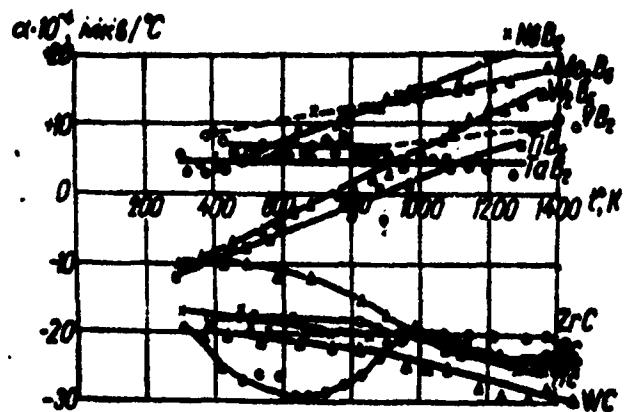
Fig.9. Temperature relation of the thermoelectromotive
force of carbides and borides.
(At top,left: microvolt/°C; at top right: Nb
equals Cb).



Fig.10. Temperature relation of thermoelectromotive
force of nitrides and silicides.
(On ordinate: microvolt/°C).

metals decreases with the growth of the acceptor capacity( i.e.,with

the reduction of the degree of shielding) of their atoms (Fig.11).This
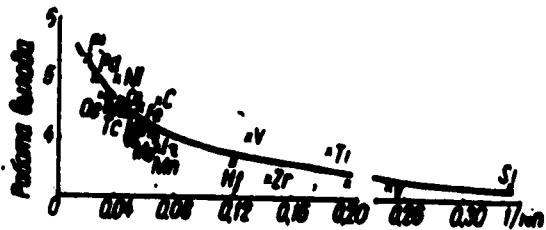


Fig.11. Relation of the work function of electrons from
transition metals to the acceptor capacity    ( $\xi$ ).
(Ordinata: work function).

is related to the growth of the perturbation effect of atomic cores

upon electron conductivity,and thus to an elevation of the level of

the chemical potential. On the contrary, for the borides of the

d-transition metals, as it can be seen on Fig.12, the work function

of electrons increases with the growth of the acceptor capacity of

the d-shell of metal atoms, which -- as it was already indicated ab-

ove -- is related to the rise in the degree of dislocation of the

electron cloud of binding toward the atomic cores of metal, also re-

lated to the statistical filling of the d-state with these electrons.

The latter leads to a lowering of the chemical potential of elec -

trons in the boride lattices,which is manifested by an increase in the work function of electrons.
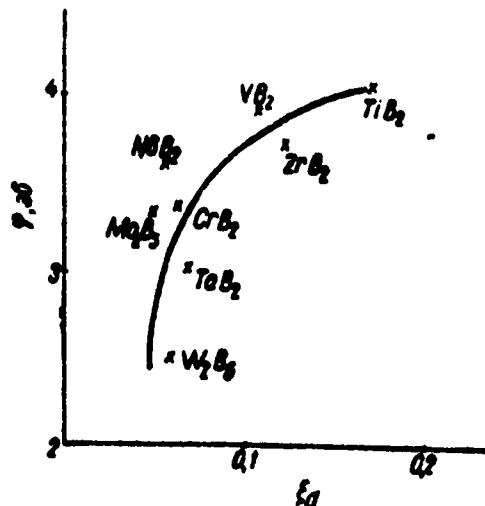


Fig.12. Relation of work function of electrons of bor-
ides of transition metals to the acceptor capacity
( $\xi$ ) of the metals.
(Ordinate: $\varphi$,3b; on graph: Nb = Cb)

G.A.Kudintsev and V.M.Tsarev [27] established that the work function of electrons from the hexaborides of the rare-earth($fd$-transitional) metals is almost monotonously growing from $LaB_6$ to $EuB_6$,and in case of $GdB_6$ it has a clearly expressed minimum, then again it increases toward $DyB_6$, and further on,it drops smoothly from $DyB_6$ toward $LuB_6$. As in case of the electric conductivity,too, this relation is connected with the $f \rightarrow d$ transition's probability /28/.

# Interatomic interaction energy and the bond strength

## in metalloid compounds

The high-grade hardness, the heat resistance, and the chemical resistance of metalloid compounds prove the considerable strength of bondings between the atoms in crystals.

G.A. Samsonov and the author [16,17,25] have computed the interatomic interaction power according to the method proposed by B.S. Sarkisov [18], and also the Debye characteristic temperature and the amplitude of the atomic thermal vibrations according to the data of experiments and literature on the thermal expansion coefficients by the method suggested by the author [19]. The obtained results are in the Table.

At considering the changes in interatomic interaction energy in case of transition from one metalloid compound to another, and the changes of the physical properties of these compounds also, it is easy to see that the interatomic interaction energy and the physical characteristics, indirectly connected with this quantity (hardness, characteristic temperature) are lowered at transition from a compound of titanium to a compound of tantalum and wolframium (Fig.13).

The interatomic interaction energy of borides does not change here monotonously, in distinction from the carbides and nitrides, which is related to the marked heterodesmia of the crystal structure of borides. Such a nature of regularity in the change of interatomic
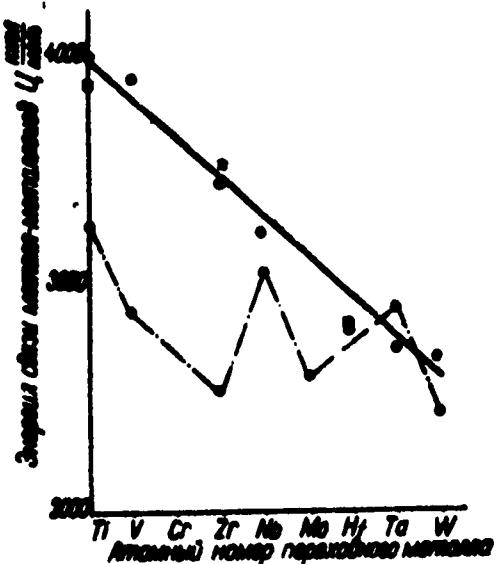
Fig.13. Change of energy of the Me - X bond with the
change of the position of the metallic components
in the periodic system:-·-·- carbides; -·-○- bor-
ides; ■ ■ nitrides.
  (Ordinate: Energy of the metal-metalloid bond,
  kgcal/mol. Abscissa: Atomic number of transi-
  tion metal).

interaction energy convincingly indicates that the unfilled d-shell

of the metal atoms plays a decisive role in the structure of metal-

loid compounds.

An increase in the degree of shielding( or a reduction in

the acceptor capacity) at transition from the top to the bottom

elements in the groups of the periodic system, or generally at a

sequence along the series Ti - V - Cr - Zr - Cb - Mo - Hf - Ta - W,

leads to an increase in the electron energy in the Me - X bonds, and

so to a loosening of this bond,which is expressed by a reduction in

interatomic interaction energy.

On Fig.14, we publish the graphs of change in the bonding en-

ergy, the characteristic temperature and the frequency of atomic vi-

brations in carbides, in relation to the criterion of the acceptor

capacity $\xi$ of the metals.

Although this relation does not seem to be monotonous, yet the

tendency toward an elevation of the bonding strength with the growth

of $\xi$ is rather clearly expressed. The symbasic change in the calcu-

lated values of bond energy and in the characteristics of the tem-
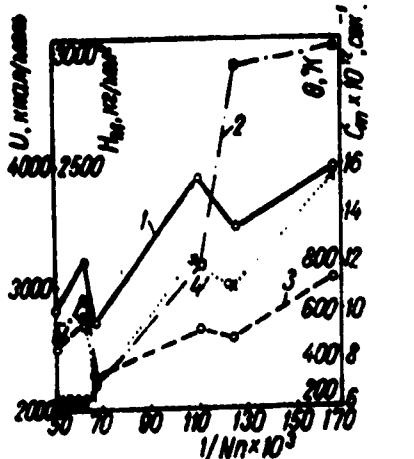


Fig.14. Relation of bond energy,hardness,characteristic
temperature and frequency of atomic vibrations in car-
bides to the acceptor capacity($\xi$)of the metals.
(Ordinata: kgcal/mol; right vertical line or sec-
ond ordinata: cm x $10^{12}$ .sec$^{-1}$).

perature and the frequency of vibrations, extracted from experimental quantities, calls attention upon itself.

The energy of the Me - X bonding in carbides and nitrides, which have simple interstitial intrusion structure, has a roughly identical value whereas in the borides which are characterized by a marked heterodesmia of the bondings these magnitudes are less, which probably is caused so that part of the valency electrons in the Me - B bonding is connected with the boron atom.

In some publications [20,21], the atomization heat is accepted as a measure for the strength of bonding in metalloid compounds, which in our opinion is not correct, since this magnitude represent in itself merely the difference of enthalpy of the components in phase and in free state of a monatomic gas, and it does not directly characterize the energy of interaction between the atoms in a solid body. From Fig.15 it can be seen that the atomization heat per one g-at(gram-atom) of the metalloid is monotonically reduced with the increase of the metalloid content in phase(the graphs are given for borides and silicides of molybdaenum), i.e., with the growth of the ground for metalloid bondings in the crystals of the compounds.

An extrapolation for a 100-per cent.content of metalloids gives the heat of their atomization. This is pointing to a decrease in the difference in enthalpy of metalloid components at elementary state, and of metalloid compounds,with increase of the number of bondings between the metalloid atoms in phases.
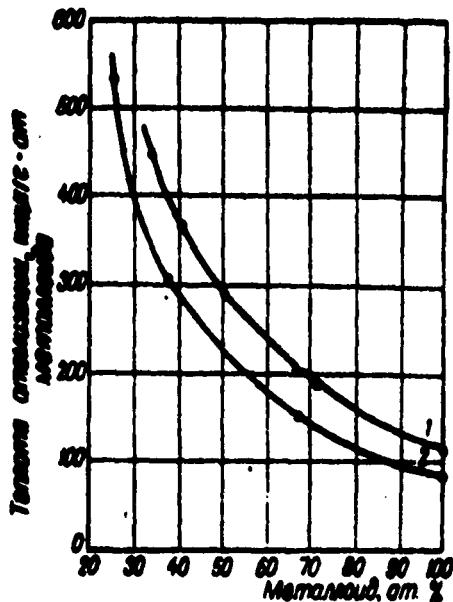
Fig.15. Relation of atomization heat per 1 g-at,of the metal-
   loid in borides(1),and silicides(2) of molybdaenum to the
   metalloid content in phase.
       (Ordinata: atomization heat of metalloid,kgcal/g-at.;
       Absciesa: Metalloid,at.per cent.)

## Physico-mechanical characteristics of metalloid compounds

The basic laws of the physico-mechanical properties of metal-
loid compounds have been formulated by the author and O.V.Samsonov
in the publication /17/.

The most characteristic property of the metalloid compounds
seems to be their high-grade hardness(See Table), related to the dir-
ectional character and the high energy strength of the interatomic

bond[9]. As it can be seen from the Table and from Fig.16, the micro-
-hardness of metalloid compounds decreases with the increase in the
atomic number of the metal components in the groups, and according
to the diagonal of the field of the periodic system occupied by the
transition metals, which is related to the reduction of the acceptor
capacity of the d-shell of atoms of the transition metals. On Fig.14,
the relation is shown between the microhardness of carbides to the
criterion of the acceptor capacity $\xi$. It can be seen that the micro-
hardness is growing with the growth of $\xi$ in the same direction as
the interatomic interaction energy and the characteristic temperature.
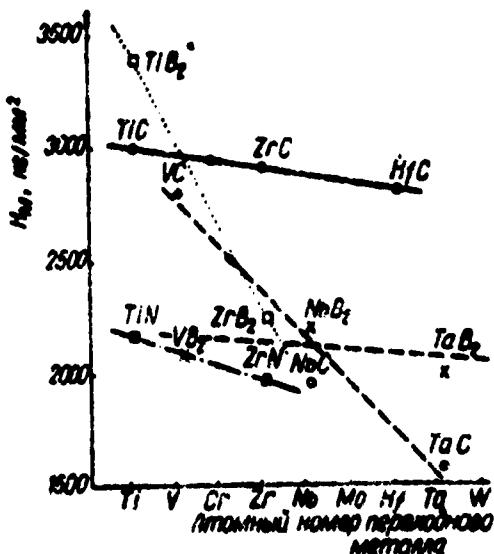


Fig.16. Relation of microhardness of metalloid compounds
to the position of the metal components in the peri-
odic system.
(Ordinata: Pressure, kg/mm$^2$. Abscissa: Atomic
number of transition metal. On diagram: Nb = Cb).

Moreover, to a substantial degree, the strength of interatomic bond,the microhardness of metalloid compounds depends upon their crystal structure.

From the Table it is evident that at transition from the cubic monocarbides CbC and TaC to hexagonal carbides $Cb_3C$ and $Ta_2C$ there is an increase in hardness, without any regard to the fact that the bonding energy for the $Me_3C$ carbides is less than for the MeC monocarbides.

In this, structure seems to have an effect upon the hardness, -- the cubic carbides have two slippage planes: (111) and (001), whereas the hexagonal carbides have only one (001). This makes difficult a plastic deformation, and it increases the hardness of these carbides.

Apparently,an analogous phenomenon takes place for the hexagonal diborides of transition metals. By comparing the microhardness of carbides and borides of the same metals, it can be seen that in those cases where the interatomic bonding energies of borides and carbides are close to the value ($U_{MeB_2}$ / $U_{MeC}$ > 0.8) ,in case of the dislocation stress of the hexagonal boride lattice whose rigidity is also elevated by the chains of boron atoms with each other, difficulties will lead to an overshoot of the hardness of borides above the hardness of carbides.

But in case of $U_{MeB_2}$ / $U_{MeC}$ < 0.8, the structural factor can not compensate for the weakening of lattice strength. In this case,the

hardness of borides shows a substantially lesser hardness than the corresponding carbides (ZrC and $ZrB_2$; TaC and $TaB_2$).

The hardness of the $MeSi_2$ disilicides is considerably less than the hardness of the borides and carbides, due to both the lesser energy lattice strength and the laminar character of structure in case of a comparatively weak bonding between the metallic layers (in comparison with borides) [22], which facilitates their dislocation stress.

Attention is called to the high values of the modulus of normal elasticity and of the modulus of dislocation of the metalloid compounds (See Table), which corresponds with a greater strength of interatomic bond.

## SOME PHYSICAL CHARACTERISTICS OF TRANSITION METALS AND THEIR METALLOID COMPOUNDS

| Phase | $T_{melt}$ °C | $H_\mu$, kg/mm² | Poisson coefficient | E, kg/mm² | G, kg/mm² | Θ, °K | $\sqrt{\bar{u}^2}_{298}$ | U, $\frac{kcal}{mol}$ | $\alpha \cdot 10^6$, g·mol⁻¹ |
|---|---|---|---|---|---|---|---|---|---|
| Ti | 1725 | 157 | 0,36 | 10580 | 3870 | 350 | 0,149 | — | 8,5 |
| TiC | 3140 | 2988 | 0,41 | 32000 | 11304 | 741 | 0,067 | 3090 | 7,42 |
| TiN | 2950 | 2160 | 0,45 | 25000 | 8821 | 517 | 0,091 | 3600 | 9,35 |
| TiB₂ | 2900 | 3370 | 0,42 | 37400 | 13107 | 615 | 0,073 | 3260 | 6,39 |
| TiSi₂ | 1460 | 870 | — | — | — | — | 0,067 | — | — |
| Zr | 1830 | 97 | 0,37 | 6970 | 2540 | 280 | 0,136 | — | 8,9 |
| ZrC | 3530 | 2925 | 0,43 | 35500 | 12369 | 460 | 0,074 | 3470 | 6,74 |
| ZrN | 2980 | 1988 | — | — | — | — | — | 3540 | — |
| ZrB₂ | 3040 | 2252 | 0,42 | 35000 | 12324 | 481 | 0,072 | 2540 | 6,83 |
| ZrSi₂ | 1700 | 1030 | — | — | — | — | 0,067 | — | — |
| Hf | 2130 | 206 | 0,37 | 8500 | 3100 | 213 | 0,127 | — | 6,1 |
| HfC | 3250 | 2600 | — | — | — | — | — | 2800 | — |
| HfN | — | — | — | — | — | — | — | 2940 | — |
| HfB₂ | 3250 | — | — | — | — | — | — | — | 5,3 |
| NfSi₂ | 1750 | — | — | — | — | — | — | — | — |
| V | 1700 | 65 | 0,35 | 15000 | 5500 | 413 | 0,124 | — | 9,7 |
| VC | 2830 | 2094 | 0,45 | 27600 | 9650 | 531 | 0,008 | 3900 | — |
| VN | 2300 | — | — | — | — | — | — | 3620 | — |
| VB₂ | 2400 | 2044 | — | — | — | — | — | 2860 | — |
| VSi₂ | 1750 | 1090 | — | — | — | — | — | — | — |
| Nb | 2500 | — | 0,35 | 16000 | 6000 | 301 | 0,124 | — | 7,1 |
| NbC | 3500 | 1961 | 0,44 | 34500 | 11946 | 470 | 0,076 | 3216 | — |
| Nb₂C | — | 2123 | — | — | — | — | — | 2570 | — |
| NbB₂ | 3000 | 2200 | — | — | — | — | — | 3060 | — |
| NbSi₂ | 1950 | 1050 | — | — | — | — | — | — | — |
| Ta | 2850 | 106 | 0,35 | 18820 | 7000 | 245 | 0,111 | — | 6,5 |
| TaC | 3880 | 1599 | 0,45 | 29100 | 10358 | 318 | 0,062 | 2770 | 8,2 |
| Ta₂C | 3400 | 1714 | — | — | — | — | — | 2390 | — |
| TaB₂ | 3100 | 2500 | — | — | — | — | — | 2940 | — |
| TaSi₂ | 2200 | 1560 | — | — | — | — | 0,073 | — | — |
| Mo | 2622 | 192 | 0,31 | 33630 | 12200 | 380 | 0,096 | — | 6,0 |
| Mo₂C | 2690 | 1499 | 0,34 | 54400 | 20268 | 461 | 0,055 | 2280 | 4,4 |
| Mo₂B | 2142 | 1790 | — | — | — | — | — | 2620 | — |
| MoSi₂ | 2030 | 1230 | — | — | — | — | 0,076 | — | 5,1 |
| W | 3377 | 360 | 0,3 | 41520 | 15140 | 310 | 0,096 | — | 4,4 |
| WC | 2600 | 1780 | 0,37 | 61300 | 22405 | 453 | 0,058 | 2760 | 3,9 |
| W₂C | 2700 | 3000 | 0,36 | 42800 | 15484 | 299 | 0,062 | 2000 | — |
| W₂B | 2770 | 2350 | — | — | — | — | — | 2470 | — |
| WSi₂ | 2165 | 1090 | — | — | — | — | 0,073 | — | — |

Note: Here, $N_m$ is microhardness; E is modulus of normal elasticity; G is modulus of dislocation; Θ is characteristic temperature; $\sqrt{\bar{u}^2}_{298}$ is the amplitude of heat variation at normal temperature; U is bonding energy; and $\alpha$ is the coefficient of expansion.

With this difference in the elasticity moduli of transition
metals and their metalloid compounds,it decreases with the decrease of
the acceptor capacity of the metal atoms,which is caused by the weak-
ening of the interatomic bonding in the compounds.

The metalloid phases are very fragile,moreover their brittle-
ness is related to the directional character,and to a much greater
rigidity of the interatomic bonds,which makes it difficult for the
elastic stresses in the material to relax. The author and G.V.Samson-
ov have shown [23,34] that the tendency of the metalloid compounds to
expand under the effect of elastic and thermal stresses is reduced
with the increase of the amplitudes of atomic thermal vibrations in
their crystal lattices, i.e.,with the reduction of the bonding rig-
idity.

Together with G.V.Samsonov and L.M.Khrenov,we made a detailed
investigation of the microfragility of a larger number of metalloid
compounds on the PMT-3 apparatus for the determination of microhard-
ness [25]. Moreover, in difference from publication [26],in this
case not only the rate of rise of the degree of breakage (crack)
of impressions was taken into account with the increase of load, but
also the character of the cracks(See the address of V.S.Neshpor af-
ter the report of Frantsevich and Pilyankevich).It was established
that the brittleness of these compounds increases in the sequence
of silicide --boride--nitride--carbide,with increase in the rigid-
ity of the interatomic bond.

The results of this work are in good qualitative agreement with the results obtained earlier by the method of studying the packing speed of the powders of hard compounds upon pressing /23/.

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# THE L$_{\beta_2}$ AND L$_{\beta_1}$ EMISSION BANDS OF COLUMBIUM IN CbN, CbC AND CbB$_2$

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For the explanation of the change of valency electrons of co‑lumbium at the formation of CbC,CbN and CbB$_2$,we investigated the emission L‑spectra of columbium,and its indicated compounds [See Note]

([Note]: Specimens for the investigations were given to us by G.V.Samsonov .)

We expound here the preliminary results of the experiments.

Spectra of the L‑series of roentgen rays were obtained on a powerfully transmitting roentgen spectrograph according to the meth‑od of Johann with the aid of a bent quartz crystal (d$_\infty$ $=$ 4246.02 X) of a radius of R $=$ 1000 mm.

In the spectrograph,a specially constructed roentgen fluo‑rescence tube was mounted with replaceable plates.

To get a great intensity of the characteristic radiation of the matter of the primary plate mirror, the cathode beam was emit‑ted under a small angle of inclination (about 28$^\circ$).

During the work of the tube, the vacuum in the spectrograph (about 10 - 5 mm Hg) was maintained by M - 1000 and MM - 40 - A pumps.

The primary and secondary plates were cooled with running water. The temperature of the secondary plate did not exceed 25°C.

The mirror of the primary plate was made of silver. The fluorescent L-spectra of Cb were excited by the characteristic radiation of the L-series of Ag.

In the L-spectra of Cb, the L lines with subscripts $\alpha_{1,2}$, $\beta_1$, $\beta$, $\beta_6$, $\beta_2$ and $\gamma_1$ as well as groups of satellite lines $L_\alpha$ and $L\beta_1$ were obtained.

On Fig.1, the microphotogram of the region of the L-series of Cb is represented, including the L emission lines with subscripts $\beta_1$, $\beta_6$, $\beta_4$, $\beta_3$, and $\beta_2$ and the reference line $K_a S$.
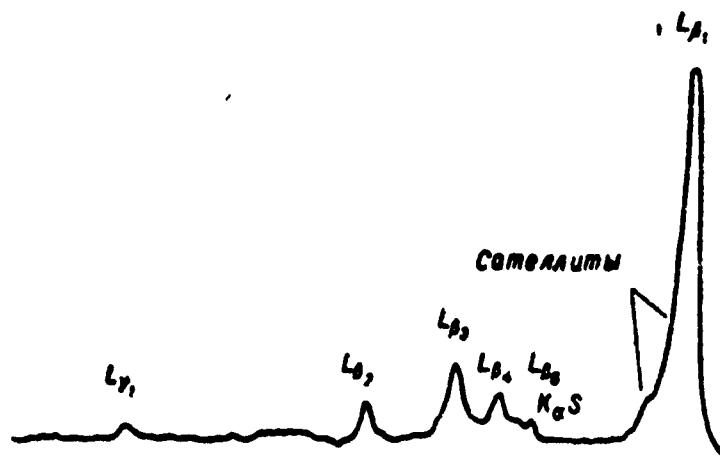


Fig.1.          (On graph: Satellites).
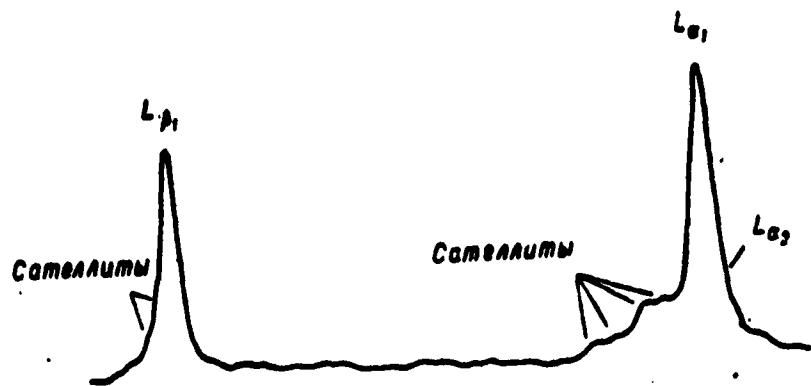
Fig.2.
(Russian word on graph:Satellites)
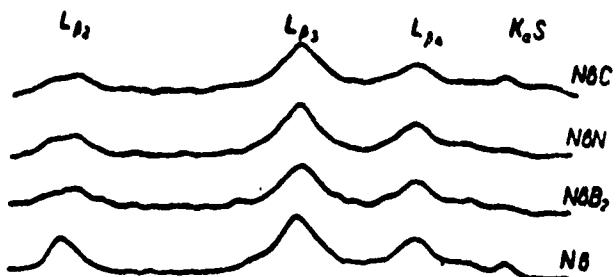


Fig.3          ( Nb = Cb)

On Fig.2,the region of the same spectrum is given between $L_\alpha$ and $L\beta_1$ .Analogous spectrograms were obtained for the L-series of Cb in the compounds CbC,CbN and $CbB_2$.

From the comparison of the obtained spectrograms it can be

seen that, at transition of Cb into a compound, different parts of the spectrum change. The shape and the intensity of the individual spectral lines and satellite lines change.

The emission bands of $L\beta_2$ and $L\gamma_1$ were more thoroughly studied.

On Fig.3, microphotograms of spectral regions $L\beta_4 - L\beta_2$ (at identical scale) of the indicated compounds and Cb were compared.

The times of exposure were so selected (for Cb...14 h, for CbC and CbN...16 h, and for $CbB_2$...17 h) that $L\beta_4$ lines were received of identical intensity.

The sharp changes in the form and intensity of band $L\beta_2$ are clearly seen. In case of pure Cb, it has a normal form of spectral line with an asymmetry index of a = 1.4. In case of CbC and CbN, it has the shape of a wide two-humped line. In case of $CbB_2$, it is markedly asymmetrical, with a very gentle drop at the short-wave side.

For the exact study of the character of changes which occurred to the $L\beta_2$ band, the microphotograms of pure Cb and of the compounds were combined.

Since the relative intensities of spectral lines changed, the question arose about the selection of a line("reference line") which should be combined with superimposition of the microphotograms.

It seemed for us that in the given case the most appropriate is to conduct the comparison by line $L\beta_4$.

1. At the transition from Cb to its compounds, changes occur in the joint band $N_{IV}, N_V, O_I$ of Cb. On this account, the relative intensity is changed for the lines which represent transitions concurrent with transitions $L_{III} \rightarrow N_{IV,V}, C_I$. Therefore, the lines $L\alpha_{1,2}, L\beta_4$, $L\beta_6$ and others cannot be used as reference lines.

2. From the non-concurrent transitions $L_1 \rightarrow M_{II,III}$ and $L \rightarrow N_{I,III}$ the $L\beta_4$ line itself represents a transition between the deepest levels, owing to which it should be the least adversely influenced by the changes in the outer shell.

Therefore, we combined the spectra of Cb and its compounds on line $L\beta_4$



Fig.4

On Fig.4, the combined region of the spectra of $Cb_4$ - CbN is presented in the region of the lines $L\beta$ - $L\beta_2$ /(the dotted line indicates the contour of the non-coincident regions of the microphotographs of pure Cb; the striping shows the portion of the band which "slipped" away from Cb). /See Note/

/Note 7: The combination of microphotograms at a given region of the spectra was carried out by way of selection of the ex-

┌posure time,and not by way of re-calculation for equal intensity.┐

As it can be seen, in case of Cb and CbN, lines L$\beta_4$ coincide along their entire contour, but line L$\beta_2$ keeps its form,and slight- ly differs in regard to intensity ( about 7 percent.)

The changes which occur to band L$\beta_3$ have different character. Band L$\beta_2$ of Cb in CbN completely enters into the lower part of the contour of band L$\beta_2$ of pure Cb. The change of band L$\beta_2$ has the same aspect as given also on Fig.4, but without the striped region,while it disappears at the nitride formation.

This permits to explain the processes,which occur at the for- mation of CbN,by the departure of a part of the electrons which are in $N_{IV}$,$N_V$,$O_I$ states of the Cb atoms.

Analogous combinations were also made for the microphotograms of Cb - CbC and Cb - CbB$_2$. The combined regions of these bands are shown on Fig.5(the dotted line refers to pure Cb; the striping is
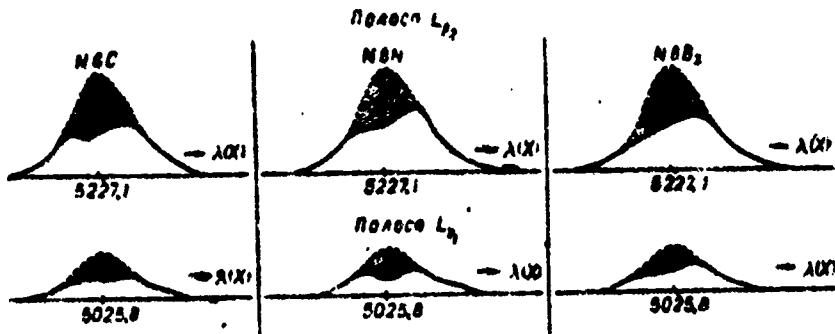


Fig.5          (On diagram,Russian word: Band; Nb = Cb)

for the band parts "slipped" away from columbium).As it is seen,in all examined compounds,the L$\beta_2$ bands enter into the lower part of the con-tour of the emission band of pure Cb.

In this manner, in borides and carbides and nitrides, the change of the L$\beta_2$ band has the character of disappearance of a part of the emission band. It is interesting to remark that in the different com-pounds different regions of the band vanish. Thus,in case of CbB$_2$, preferably the short-wave part vanishes. In carbide and nitride,prefer-ably the central part disappears.

Since the emission band seems to be complex,expressing the states $N_{IV}$,$N_V$ and $O_I$, such changes can attest that,in the different compounds, electrons of different states take part in different ways in bonding.

In Table 1,the numbers are given which characterize the chan-ges of band L$\beta_2$ in pure Cb and its compounds.

TABLE   1.

Таблица 1

| Вещество | $r^\circ$ | $1-r$ |
|---|---|---|
| NbN . . . . | 0,715 | 0,285 |
| NbC . . . . | 0,729 | 0,271 |
| NbB$_2$ . . . | 0,685 | 0,315 |

(Column heads: 1...Substance; 2(Note): r is equal to the ratio of the area of L$\beta_2$ of the compound and of columbium)

Analogous changes occur also in band $L\gamma_1$. In Fig.6,we present the combined $L\gamma_1$ band of the compounds and pure Cb (as in case of band $L\beta_2$ ,the combination also was made at identical intensity of line $L\beta_4$).
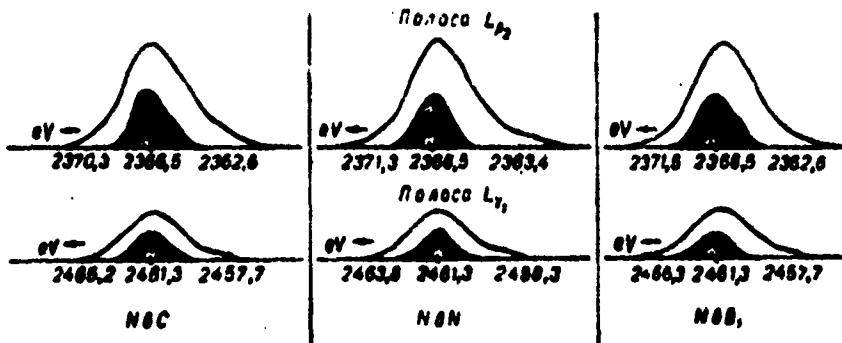


Fig.6                    (Russian word on diagram:Band;
                         Nb = Cb)

It can be seen that the change in band $L\gamma_1$ is similar to the changes in band $L\beta_2$, i.e., there seems to be a departure of its various parts.

In Table 2,we give the numbers which characterize the change in band $L\gamma_1$ for pure Cb and its compounds.

The comparison of the slipping part of bands $L\beta_2$ and $L\gamma_1$ is also presented on Fig.6.

The data of Table 1 and 2 as well as Fig.6 show that in concrete substance the changes in bands $L\beta_2$ and $L\gamma_1$ are not entirely similar.

TABLE 2.

| $1$ Вщество | $r$ | $1-r$ |
|---|---|---|
| NbN . . . . | 0,703 | 0,297 |
| NbC . . . . | 0,739 | 0,271 |
| NbB$_2$ . . . | 0,740 | 0,260 |

$2 \bullet r$ равно отношению площадей
L$_{\gamma_1}$ соединения и ниобия.

(Column headings: 1...substance; 2...$r$ is equal to the ratio
of the area of L$\gamma_1$ of the compound and of Cb).

This difference seems to result apparently so that L$\beta_2$ is
caused by transition into the states S$_{1/3}$,d$_{3/2}$,and d$_{5/2}$, but for
L$\gamma_1$ only by transition into S$_{1/3}$ and d$_{3/2}$ .

It should be assumed that the different form of bands L$\beta_2$
and L$\gamma_1$ ,in the different compounds of Cb, is due to the fact that
the specific weight of states d$_{3/2}$ and d$_{5/2}$ in the common band are
different.

The specific weight of states d$_{3/2}$ and d$_{5/2}$ in the common
band can be limited by the assumption that the part of transitions
to state S$_{1/3}$ in emission bands L$\beta_2$ and L$\gamma_1$ is small in comparis-
on with d$_{3/2}$ and d$_{5/2}$(in the heavier atoms the intensities of lines
L$\beta_7$ and L$\gamma_9$ form not more than 2 percent. of the intensities of
lines L$\beta_2$ and L$\gamma_1$).

In the supposition that the intensities of lines L$\beta_2$ and
L$\beta_1$ and L$\gamma_1$ satisfy the formula:

$$I\beta_2 : I\beta_{1,5} : I\gamma_1 = 6\frac{N_{5/2}}{N_{3/2}} = 1:5 \; ,$$

where $N_{5/2}$ is the number of $d_{5/2}$ states; $N_{3/2}$...the number of the $d_{3/2}$ states, from the experimental data for the ratio of intensities of the $L\beta_1$ and $L\gamma_1$ bands, the ratio of $N_{5/2}:N_{3/2}$ can be determined.

Below are given the data calculated according to the given formula of the $N_{5/2}:N_{3/2}$ ratio, and with our experimental values

| Substance | Nb=Cb | CbN | CbC | CbB$_2$ |
|---|---|---|---|---|
| $N_{5/2}:N_{3/2}$ | 2.08 | 2.10 | 2.08 | 1.90 |

( /¯Note_7: For the filled levels, $N_{5/2}:N_{3/2} = 6:4$, and the quoted correlation ratio is transformed into the Burger & Dorgel rule .)

## Conclusions

1. The L-series of Cb was investigated in compounds CbN,CbC, and CbB$_2$.

2. It was found that while the intensity and the shape of lines $L\alpha_{1,2}$, $L\beta_1$, $L\beta_4$, $L\beta_3$ and so on, changes a little, the intensity and the shape of bands $L\beta_2$ and $L\gamma_1$ undergo a sharp change.

3. Bands $L\beta_2$ and $L\gamma_1$ of Cb in the compounds are only parts of the corresponding bands of pure Cb.

4. The conducted measurements are not accurate enough for reliable quantitative conclusions; however, undoubtedly in case of Cb, the departure of the d-states in compound CbB$_2$ is larger than in CbN and CbC.

## Questions and answers

Q: What conclusions do you make as to the bond types in car_
bides,nitrides and borides?

Ya.E.Genkin: In order to make any conclusions, both compounds
(components) of the system must be thoroughly investigated. In our
case,we examined only the Cb in the compounds. The second component
and all its properties must be also examined. Any kind of conclusion
can be made only then.

Q.: How do you explain the splitting of the $L\beta_2$ band of Cb
nitride and carbide? Why does this band differ from the band in di_
borides?

Ya.E.Genkin: One cannot say that the $L\beta_2$ band is split,be_
cause line $L\beta_2$ does not seem to be a strictly dispersed line,guard_
ing the state of the internal filled levels. It seems to be a com_
plicated complex of transitions — at $N_4,N_5$ and $O_1$. Therefore,we can
not say that it is two separate lines. Splitting can happen if some
information is available on the character or energy of this or an _
other line.

Here,however,we have a band. Therefore, we are forced to
speak of it as a whole. At successfully selecting the criteria of
the combination of the $L\beta_4$ lines,we endeavoured with all effort to
make it such that the $L\beta_4$ lines should coincide. Then,it was found
that the edge of band $L\beta_2$ coincides with the recession of pure Cb

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line. Therefore, we say that as a whole the energy of this band generally did not change. It seems to us that we should not say that the energies of the lines are different ( as allegedly the splitting of the lines seems to be). And if the energy remained one and the same, then the probability of a transition is here also constant. Only the number of transitions in the given state has changed. It is interesting that no kind of edge, i.e., electron of an arbitrary energy, slips, but separate parts of the band are slipping. This is a proof that the whole $L\beta_4$ band has zones $N_4, N_5, O_1$ with overlapping. We can say that these transitions are already not in columbium.

In the limits of this band, the $O_1$ transitions are little expressed. We are not able in every case to distinguish them. Therefore all discussion about their transitions is approximative; we cannot judge the splitting with precision.

There is still this question:— in case of compounds, can the decrease in the relative intensity of the $L\beta_2$ band (by comparison with pure Cb) be explained only by the decrease in the number of the free states?

It seems to us that particularly since the energy does not change, the probability of transitions does not change either. But the fact that a part of the line is eliminated, proves especially that they are absent.

<u>Discussion on the Report of M. I. Korsunskiy and Ya. E. Genkin</u>

<u>A.Z.Men'shikov</u> (Institute of Metals Physics, AN SSSR):

From our point of view, the following interesting results were reached by the discussed work:

1. For all investigated compounds and pure Cb, in the scale of energies the position of the $L\beta_2$ band remains unchanged.

2. In diboride, carbide and nitride of Cb, the relative intensity of the $L\beta_2$ band is less than in pure Cb.

The first experimental result permitted the authors to announce for all compounds the hypothesis on the constancy of probability of transition from the $\underline{d}$ and $\underline{s}$ symmetry levels to the $\underline{p}$ symmetry level. Then, according to the formula $I(E) \sim P().n(E)$, the reduction of the intensity of the $L\beta_2$ band can be explained only by the decrease in the density of the occupied states, i.e., by less number of transitions, which gave the right to the authors to calculate the number of electrons at the levels according to the relative intensity of the $L\beta_2$ band.

However, in our opinion, this kind of calculation does not determine the veritable position of things. The point of matter is that CbC and CbN have a crystal structure of the NaCl type, and we should have here $d^2sp^3$-hybridization of the wave functions. But the possibility of hybridized $\underline{spd}$-states can lead to a change in the probability of transition from the states which condition the existence of the $L\beta$-band.

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Therefore, here the calculations of the electron number at the states according to the methodology elaborated by the authors, is open to doubt. Of course, the significance of the factor of diminution of the electron number at the $\underline{d}$ and $\underline{g}$ symmetry levels is by no means belittled, the less so because the existence of an ionic covalent type of bonding can be here surmised.

# X-ABSORPTION SPECTRA OF CHROMIUM IN BORIDES,CARBIDES,NITRIDES AND SOME OTHER COMPOUNDS

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AN SSSR

The solid compounds of refractory metals generally, and the
intrusion phases in particularly find a wide practical application
in engineering since they are characterized by an interesting collec-
tion of physical and chemical properties: -- high temperature of
melting,great hardness,brittleness and good electric conductivity.
The originality of the crystal structures,the complexity of the el-
ectronic structure,and the character of the interatomic bonding for-
ces make these compounds one of the interesting objects of research.

Inspite of a large number of publications,whose review is well
presented in the monographs [1,2],the problem about the character of
interatomic interaction in the intrusion phases continues to remain
obscure.Later, attempts have been made at solving this problem by
the method of roentgen spectroscopy [3 - 6],one of the most direct
methods of studying the electron structure of solid bodies.

In the present work, we give the results of study of the nature of interaction between the atoms of a metal of the transition group and the metalloids of the first series of Mendeleyev's Table(B,C,N,O).

The continuous change of bond type from the metallic(in beryllides) through the covalent(in carbide) to the ionic(in oxides) was presented in the publications $[6,7]$, and further developed in detail by G.V.Samsonov $[8]$.

As object of research, from among the metals of the transition group, chromium was taken in its borides, carbides, nitrides and oxides ($CrB, CrB_2, Cr_3C_2, Cr_7C_3, Cr_2N, CrN, Cr_2O_3$) and the chemically pure substances of $CrCl_3$, and $Cr_2(SO_4)_3$.

The borides and carbides were obtained in the Institute of Metal Ceramics and Special Alloys of the AN USSR. The nitrides were obtained by diffusion saturation of Cr in ammonia jet by the methodology of $[9]$. $Cr_2O_3$ was obtained by oxidation of electrolytic Cr at $1000^{o}$C in free air.

The roentgen K-edge of Cr absorption was investigated on a spectrograph with focussing according to Johann in the first order of reflection from plane(1340) of a quarts crystal. As line of comparison, the $K_{\alpha 1}$ line of Fe and the $K_{\alpha 2}$ line of Mn were used. The linear dispersion was 2.5 XB/mm. The tube worked at 12-13 kV, 45-50 mA. The survey's length was 35-40 hours.

The Cr absorption spectra seemed to be of the greatest contrast at 5-6 mg/cm$^2$ absorber density. Not less than three spectra

were made for each substance.

For all phases investigated by us, we measured the magnetic sus-
ceptibility. The measurement was carried out   (by P.G.Rudomanov) on
magnetic balances with a field of 8600 oersteds and at 17°C. Seasalt
was used as standard.

The figure(unnumbered) represents the basic K-edge of Cr absorp-
tion in the examined compounds and metallic Cr. Along the abscissa,the
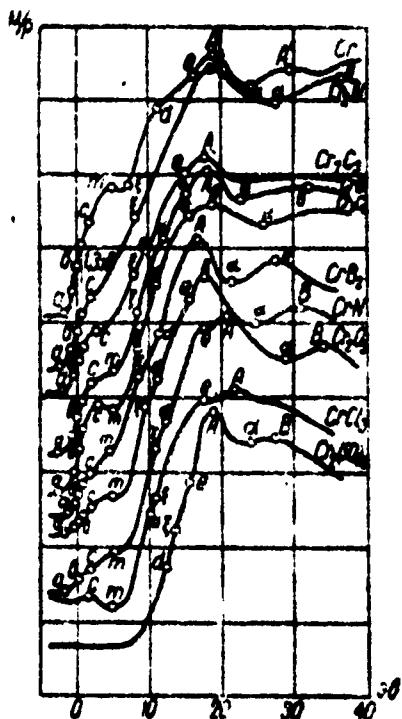
Fig.(No legend; on abscissa: electron volts)

energy(power) is laid out in eV-s, by counting from a chosen zero,and
along the ordinate the magnitudes are proportional to the absorption
coefficient.

According to Beeman and Friedman [10],the first region of the
K-absorption spectrum of transition metals with open 3d-shells(in par-
ticular, for Cr $3d^5 4s^1$) is conditioned by transitions of 1-s-elec-
trons(one-s) into the unoccupied part of the generalized 3d-4s band
with admixture of the 4p-state.

The top curve on the figure illustrates the change of absorp-
tion coefficient in the region of the main K-edge of the electrolytic
Cr. It can be seen that the first region of absorption does not have
an arc-tangent-shaped form,but it possesses a certain kink at Point
C. By analogy with the curves of K-excitation, obtained by the iso-
chromatic method of the characteristic spectrum [11],this kink can
be also explained by transitions of Cr into the 3d-state.

And now, the first initial region of absorption in pure Cr is
conditioned by transitions of K-electrons into the 3d and 4s bands,
and it exactly reflects the transitions into those states which un-
dergo changes in relation to the type of the chemical bond. But
since the absorption coefficient itself depends upon the density of
unoccupied states and on the probability of transition at these
states,i.e., $I(E) \sim P(E)n(E)$, these two factors will influence the
intensity of the initial absorption.

The experimental curves presented on the figures are arranged

in such an order that along the edges the curves are arranged for sub-
stances of different bond types, i.e., Cr with metal bond, $Cr_2(SO_4)_3$
with ionic bond. From the examination of these curves it follows that
in pure Cr the initial absorption by intensity is roughly one half of
the whole absorption discontinuity, while in $Cr_2(SO_4)_3$ it is entirely
not; moreover, the energy position of the A maximum remains unchanged.

Consequently, in the given compound of trivalent Cr,the quasi-
atomic 3d-4s levels are considerably free. However,due to the weak
interaction between the neighboring Cr ions in $Cr_2(SO_4)_3$ crystal,
the overlaps of 3d and 4s bands with the 4p band are either entirely
absent,or very small. Hence,the probability of transition of a K-
-electron into the 3d-4s-state is markedly reduced,which is manifest-
ed in the disappearance of the initial region of absorption in the
pertinent spectrum. The given example shows how large the effect of
transition probability is upon the intensity of the initial absorp-
tion.

On the transitions in the following three compounds($CrCl_3$,
$Cr_2O_3$,CrN) I remark that in these compounds the fine structure of
the basic K-edge of Cr absorption gets richer. The initial absorp-
tion,appearing in $CrCl_3$,gets larger in intensity in oxide,and still
larger in nitride. The crystal structure of the given compounds of
the group has an octahedral atomic coordination. According to Kim-
ball [12],a $d^2sp^3$ hybridization of wave functions should here ap-
pear.It is thought that due to such a hybridization of ds-functions

with p-functions,the probability of K-electron transition into the
3d-4s-state is larger.

An interesting peculiarity of the K-absorption spectra of Cr
in the given compounds of the group -- shown the first time in this
work,as we think -- is the presence of fine structure in the initial
region of absorption(in the figure,the kinks in the initial region
of absorption are suitably designated by Points c and m).

As to the character of absorption spectrum, the diboride($CrB_2$)
is close to these compounds. It has a somewhat different atomic coor-
dination(the Cr atom is within a hexagonal prism on whose apex the B
atoms are arranged).

Results of the magnetic susceptibility measurement,given in
the following Table,indicate that in the order of the compounds
$Cr_2(SO_4)_3$,$CrCl_2$,$Cr_2O_3$,CrN,$CrB_2$,its value diminishes from $28.0 \times 10^{-6}$
to $9.0 \times 10^{-6}$ cgsm,which proves the diminution in the number of un-
compensated electron spins in the 3d-shell of the Cr atoms.

The presence of a regular change in intensity of the initial
absorption as well as the data on the magnetic susceptibility measu-
rement make us believe that in this series of compounds,together
with the ionic type of bonding,there is a rising covalent compo-
nent of interatomic interaction.

In comparison with the first, the second group of compounds
($Cr_3C_2$,CrB,$Cr_7C_3$,$Cr_2N$) has a larger initial region of the K-absorp-
tion spectrum, equal roughly to 25-30 percent. of the whole absorp-

tion discontinuity,and a magnetic susceptibility(See Table) in the
order of (5 to 6) x $10^{-6}$ cgsm,which is substantially less than the mag-
netic susceptibility of the preceding series of compounds. The exam-
ination of the crystal structure in the given compounds finds the pres-
ence of more or less distorted prismatic atomic coordination for
which according to publication [12] there should be a $d^4$sp or $d^5$p
hybridization of wave functions present.

TABLE.

| 1 Вещество | 2 $\chi \cdot 10^{-6}$, ед. CGSM | Электронная конфигура- 3 ция | 1 Вещество | 2 $\chi \cdot 10^{-6}$, ед. CGSM | Электронная конфигура- 3 ция |
|---|---|---|---|---|---|
| $Cr_2(SO_4)_3$ | 28,0 | — | $Cr_3C_2$ | 6,4 | $d^4$sp или $d^5$p |
| $CrCl_3$ | 21,8 | $d_6sp^3$ | $CrB$ | 6,7 | $d^4$sp или $d^5$p |
| $Cr_2O_3$ | 19,2 | $d^6sp^3$ | $Cr_7C_3$ | 3,8 | $d^4$sp или $d^5$p |
| $CrN$ | 18,0 | $d^6sp^3$ | $Cr_2N$ | 5,8 | $d^4$sp или $d^5$p |
| $CrB_2$ | 9,0 | — | $Cr$ | 3,4 | — |

(Column headings: 1...substance; 2...unit in the cgs sys-
tem; 3...electron configuration; 4..."or").

If only the presence of a covalent type of bonding is assumed,
then the given compounds should be diamagnetic or slightly magnetic,
and the initial region of the K-absorption spectra of Cr in these
compounds should either entirely vanish,or it should be small in
magnitude. In our case,neither one nor the other happens.Hence,the
nature of the bonding forces seems to be complex in these compounds,

and ,from our point of view,it rather agrees with the idea of the resonant covalent bond developed by Pauling $\boxed{13}$.

With a general examination of the K-absorption spectra of Cr in pure Cr and its compounds of boride,carbide,nitride,oxide,chloride, the invariability of the position of Point $\underline{b}$ in the energy scale should be noted,independently from the type of compound. The kinks of the absorption coefficient curve,corresponding to Points $\underline{d}$ and $e_\perp$ whose nature we do not study,as well as the $\underline{A}$ maximum are subject to changes both in the energy scale and in the intensity scale.

Point $\zeta$(zeta) $\zeta = \left( \dfrac{A - a}{2} \right)_{\mu\varphi}$ --- the middle of the absorption discontinuity -- is regularly shifted to the short-wave side by the extent of increase of the ionic component of bonding force in the compounds.

## Conclusion

1. The nature of the interaction of Cr atoms with the metalloid atoms of the first line of Mendeleev's Table(Cl,O,N,C,and B) continuously changes from ionic covalent to covalent metallic.

2. The obtained experimental results indicate that the different compounds inside one diagram of state cannot pertain to single type of bonding forces,because in this case the concentration of metalloid can play an essential role. This is particularly characteristic for the compounds  CrN and $Cr_2N$, $CrB_2$ and CrB.

3. A hypothesis on the metallic state of the metalloid atom (as this is correct in case of the Pd-H system) cannot be extended

to all classes of the Haggian phase of intrusion. The typical intrusion phase of CrN is close to $Cr_2O_3$ by nature of the interatomic interaction, and in this oxide the bonding forces have ionic covalent character.

4. In the metalloid compounds, the character of bonding forces is complex. Of course, the ordinary classification into ionic, covalent and metallic type of bonding is not in agreement with reality.

The authors express their deep gratitude to G. V. Samsonov for the permitted samples and his great interest in the work.

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Discussion on the report of S.A.Nemnonov and A.Z.Men'shikov

E.A.Zhurakovskii(Odessa Pedagogical Institute ):

The question about the nature of forces of chemical interac-tion between atoms of a metal and metalloids in the carbides, ni-trides and other intrusion phases of transition elements presents great practical interest,and for many years it has attracted the attention of investigators. Nevertheless,until now it still has not been sufficiently explained. For the foundation of present as-sumptions,magnetic,electric,and crystallo-chemical data are used. However,until recent times,information on the roentgen spectra of the atoms in these compounds was not available which,in differ-ence from the data of all other methods, could give the most direct information about the energy state of atoms in these compounds.The

first investigations by emission spectra in this area were made re -
cently by E.E.Weinstein and coworkers.

The solution of this problem is also the purpose of the pres-
ent work in which the fine structure of the roentgen K-absorption
spectra of Ti is investigated in the alloys of the Ti-C system where
the metalloid content changes from 24 to 9 percent. by weight.

All investigated alloys were prepared by the methodology des-
cribed in the literature, and (except the 9-percent.alloys) they per-
tain to the same field to which the carbide of face-centered cubic
lattice belongs.

The research was conducted on a spectrograph specially cons-
tructed for this purpose,whose construction was suggested by I.B.
Stary,and described earlier.

The plane of a quartz crystal prism was used as analyzer. The
method of recording the spectra was photographic. The optimum den-
sity of the absorber was experimentally selected. It was equal to
5 mg/cm$^3$. At higher densities of the absorber, the fine structure
of the K-edge of absorption was less clearly observed at the ex-
periment.

For comparison,parallel with the carbides, the fine struc-
ture of the K-absorption edge of Ti and its dioxide(rutyl) was in-
vestigated. Attention was called to the fact that the energy,cor-
responding to the maximum of the long-wave absorption band of Ti,
remained unchanged in both compounds of this metal. This is in good

agreement with the phenomenon found in the preceding researches, and it does not agree with the hypothesis that at the formation of the carbides of transition elements a "metallization" of the bond occurs, which would be manifested by a partial filling of the 3d-energy levels of the transition metal atoms. More detailed experimental investigations will be continued in the very near future.

V.S.Neshpor (Institute of Metal Ceramics and Special Alloys,AN USSR):

Something should be said in connection with the communication on roentgen spectral research of the metalloid phases. As a direct method of studying the character and strength of bonds in metals and in compounds,these researches are of great interest.Yet,their de - tailed examination remains still a failure until now. The data of individual researches occasionally disagree with each other, and they are being arbitrarily treated by one school or the other.

Therefore, it seems to me that according to the results of researches of a number of physical characteristics of these substances,such a structural model could be now roughly presented for these compounds on whose basis the separate spectral data could be dealt with.

While talking of electron transitions to this or to that side, they cannot be examined only from the point of view of the zonal theory, but the individual peculiarities of the structure of atom components of the compounds must be studied. Undoubtedly, the greatest effect upon the physical properties of metalloid compounds is

exercised by the degree of filling of the 3d-shell of the transition metal atoms and the ionisation potential(or electro-negativity) of the metalloid atoms. These factors determine the density of the occupied states both in the valency zone and in the conductivity zone, and hence they show a substantial effect upon the position and intensity of the spectral lines of metals in compounds, particularly in case of the L-series.

The type of crystal structure and the number of bonds should be also studied.

From the results of the work reported by M.I.Korsunskii and A.Z.Genkin, it can be seen that the greatest number of electrons leaving the metal are in boride($CbB_2$), and a less number in nitride and carbide, which corresponds to a larger number of B bonds in the boride lattice($6Me-B$ and $3B-b$) than the number of C and N is in the carbide and nitride($CMe-X$). In nitrides, the metal loses more electrons, in correspondance with the greater electro-negativity of N, than in case of carbide which has a smaller electronegativity of C.

The researches of the initial absorption region in ionic and metalloid compounds are of considerable interest. But, at the end, one cannot agree with the conclusions drawn in this work as to the transition from the purely ionic Me - X bond in chloride and sulphate to the covalent bond in borides, carbides and nitrides.

Researches of the temperature relation of electric conductivity of the latter phase, presented in our report, indicate the metal-

lic nature of conductivity of the transition metal carbides and borides
i.e.,the presence of free carriers of electric current in them,subordi-
nated to the Fermi-Dirac statistics.

Thus,it is apparently correct to consider the changes in the re-
gion of initial absorption in the compounds investigated by S.A.Nemno-
nov and A.Z.Mer'shikov as result of subsequent gradual transference of
the density maximum of the electron shell in the Me - X bond from metal-
loid to metal in the sequence of sulphate(chloride) - oxide - nitride -
carbide - boride,which is also pointed out in our report.

In our opinion,such a model also fits the results of the work
of Vaynshteyn and Vasil'yev according to the examination of the K-emis-
sion spectra of Ti compounds. The growth of the metallicity of com -
pounds also happens to be in this direction.

M.D.Glinchuk (Institute of Metal Ceramics and Special Alloys,AN USSR):

Investigation of the behavior of admixture in solid solutions
is of considerable interest. I wish to touch on the problem of the ef-
fect of the admixture's concentration upon the energy spectra of the
base metal.

In works of foreign authors and in recent works of the Soviet
scientists Gurov and Borovski,it was shown that change in the admix-
ture's concentration effects the shift of the Fermi state of the base
metal. For each base metal,a certain definite concentration exists
below which the dislocation of the Fermi level can be disregarded.

At concentrations above this definite one, due to interaction of the admixtures,the shift of the Fermi level considerably increases. Thus,if the basic solution is copper,then with the admixture's concentration of an excessive single charge of about 50 at.percent.,the Fermi level shift is roughly about 0.5 eV(according to the data of Friedel,Advancements of Physics,1954)

We were interested in the solid solutions on iron base. In transition metals(i.e.,with larger effective masses) the excess charge of admixture is quickly shielded.

Therefore,the solved elements mutually interact only when the concentration of admixture is sufficiently large. For iron,the concentrations must be more than 60 at.percent. With smaller concentrations,the Fermi level can be considered practically unchanged.

Redistribution of the excess electrons among the open 3d and 4s shells of iron occurs on account of electron scattering at thermal vibrations of the crystal lattice of the base metal. As the researches of a number of authors show, the electron fraction of those which slip out into the d- and s-bands,should be proportionate with their relative level densities in the vicinity of the Fermi surface.

Since the density of d-state is larger than the density of the s-state,the larger part of the excess electrons must go for the building of the d-band of the base metal.

M.I.Korsunskii(Kharkov Polytechnical Institute):

I would like to make a few comments.

In their report,S.A.Nemnonov and A.Z.Men'shikov emphasized the great possibilities of roentgen spectral analysis.With this method it should be in agreement that it gives good basis for the judgment of the electron behavior in the various states. From these data then, conclusions are drawn on the electric conductivity of the substance and on its other properties.

However, as I.I.Frantsevich correctly remarked,the chemical compound must be investigated in a complex manner, i.e.,the spectral method must be combined with other methods of research.

What is then trustworthy in the discussed report and what causes doubt?

The data entered in Table are particularly informative. They can undergo some changes in this way or another. These data,as the spectral curves themselves also, were obtained in a hurry; their methodology of processing was also developed literally in a few days.

Therefore,these data should be considered as approximative.

I wish to call attention to those additional possibilities which this method reveals. It seems to me that firstly in the roent-gen spectral practice there is a possibility to determine the number of electrons which leave for bonding.

Particularly interesting are,undoubtedly,the results of study-

ing the effect of concentration changes in the range of the area of

homogenouaness of the metalloid phases of the type of nitride,car-

bide,boride and other compounds.

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# COMPARATIVE BRITTLENESS OF HEAT-RESISTANT COMPOUNDS

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Articles from refractory compounds of the type of carbides ,

borides,nitrides and silicides,more and more widely used in contem-

porary engineering,should possess sufficient stability against a ther-

mal shock. The realisation of this property in material which has

high strength of atomic bonding,low capacity of relaxation of inter-

nal stresses,and which are brittle by their nature,is extremely dif-

ficult,and is not always feasible.

The attempt at preparing and investigating the details for the

basis of the refractory compounds indicates that,regardless of their

apparent identical brittleness and resistivity to the action of nor-

mal tensile forces,they react in different way to thermal shock,

which proves their considerable difference in regard to brittleness

and relaxation capacity.

However,since these materials possess identical macroscopic

brittleness,as mentioned above, for appropriate selection of those among the refractory compounds which could serve as basis for the preparation of super-refractory materials resistant to heat shock,it seems to be necessary to resort to microscopic research for the study of their comparative properties at small scale.

Therefore,we have undertaken a comparative microscopic investigation of the mechanism of destruction and brittleness in relation to the potential capacity of resisting the action of thermal shock. In these researches we used 1) the method of constructing statistical curves of microbrittleness by the cracking ability of the impressions caused by the microdurometer's indentor at different loads, and 2) the method of electron microfractography.

Regardless of the extraordinary importance of the estimation of comparative brittleness of refractory compounds,until now a sufficiently clear,simple and reliable method has not been available for such an estimation.

Various methods have been proposed for the comparison of the brittle properties of refractory compounds: -- by compressibility of powders [1], by the number of hits upon the sample which cause destruction [2], by the work spent on deformation of material at obtaining an impression by the durometer [3], and others.

Let us stop a while for the detailed description of the latter method. By this method, a relationship is built between the number of impressions which have cracks and the magnitude of the load,

and that $P_k$ load is determined by which 50 percent of the impressions will crack. At the determination of hardness N, the diamond prism of the indentor does some work spent on plastic deformation of the material. This work is computed for force $P_k$. By knowing $P_k$, the hardness N, and the apical angle of the pyramid, the work $S_k$, called by the author [2] "viscosity", can be calculated. For Bickers' pyramid the formula is:

$$S_k = 2 \times 10^{-4} \sqrt{\frac{P_k^{\,3}}{H}} \quad [gcm].$$

From our point of view, the greatest prospect has the so-called microbrittleness method which, as it is known, consists of the construction of curves which are related to the number of impressions that crack under the indentor of the microdurometer from the load put upon the indentor, or -- after reaching the load at which all impressions have cracks, -- the number of cracks in one impression with a certain load magnitude [4,5]. Moreover, obviously at a given load, the more brittle materials will have a larger number of impressions with cracks( or correspondingly, fewer uncracked impressions). Thus, by the comparison of the curves of mircobrittleness, we can also judge the relative brittleness of the investigated materials.

We constructed such curves for a number of refractory compounds and silicon which enters into some fire-resistant composi - tions:- they are given in Fig.1. On the micro-sections prepared by diamond powder, the measurements were made on a PMT-3 apparatus for
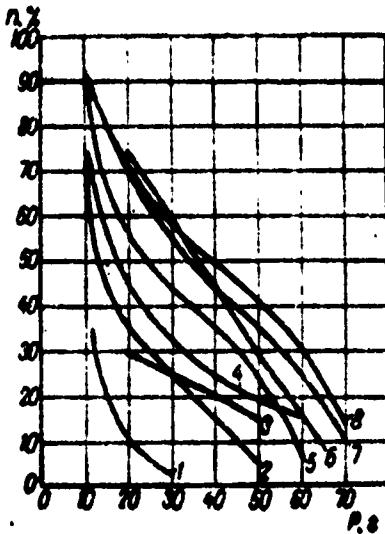
Fig.1.Curves of microbrittleness for several refrac-
tory compounds and silicon: 1...silicon; 2 ...
$CbB_2$; 3...TiN; 4...SiC; 5...ZrC; 6...TiC; 7...
$CrB_2$; 8...$Cr_3C_2$.
(Abscissa: Pressure ,in grams)

the determination of micro-hardness. Data obtained from 50-70 measure-

ments enter into one point of the curve. The reproducibility of the

data,obtained in the two halves of one and the same sample,is ± 5%

which apparently can be considered as the accuracy of the method it-

self,and can characterise the satisfactory degree of its objective-

ness.

At the scrutiny of the microbrittleness curves,first of all

the fact is noted that several curves intersect each other,for ins-

tance for $Cr_3O_2$ and TiO, for ZrC and SiC.

This brings a certain disorientation into the problem of determination of comparative brittleness,since in case of small loads,e.g., ZrC proves to be less brittle than $\beta$-SiC,but with larger loads the opposite happens.

The question arises,what should then characterize the comparative brittleness of materials:-- mutual situation(i.e.,the run of the curves); the start of the curves,i.e., the load at which the impressions start to crack; or their end, i.e., when all impressions have cracks?

From Fig.1 it is evident that the maximum load at which cracks are still not formed around the impression differs very little for the different materials so that apparently this magnitude cannot be considered characteristic.

As to the mutual situation of the curves,obviously we should take here in account the behavior of the separate grains of tested material. Under actual conditions of a multicrystal sample,a grain which is subjected to the action of the indentor will be under conditions of a disproportionate allround compression,particularly when we take in account that the refractory compounds are destroyed in the area of elastic deformations [6]. Evidently,therefore,the field of stress where the tested grain is located will depend upon different factors,e.g.,on granularity,presence of internal stresses and

so on. In agreement with this, the grains of the material tested for micro-brittleness will behave in different ways, since they will be in different force fields. This will also cause that for the different materials the curves of microbrittleness go different ways, especially that they intersect. To be able to compare the different curves with each other, we must know how their course is influenced by the field of stress in the sample.

For the estimation of this influence, we calculated the relative derivative

$$\propto \ = \frac{P}{n} \cdot \frac{dn}{dP}$$

along each curve, and constructed the relation of this magnitude to the load. In this formula, $\underline{P}$...is the load at which the number of non-cracking impressions is $\underline{n}$ (percent.). The derivative is calculated at the point which is characterised by the given values of $\underline{P}$ and $\underline{n}$. The obtained relations are shown in Fig.2.

From Fig.2 it is evident that the majority of the examined materials are characterized roughly by an identical $\propto$ derivative within the range of 20-40 grams of load. At larger loads, the curves $\propto$ = f(P) begin to differ markedly. In our view this proves that, as to brittleness, materials can be compared by the run of the curves $n = f(P)$ only within the limits indicated by us, and at roughly identical values of $\propto$ . Moreover, the samples must be evidently of identical granulation. The most reliable results should be obtained
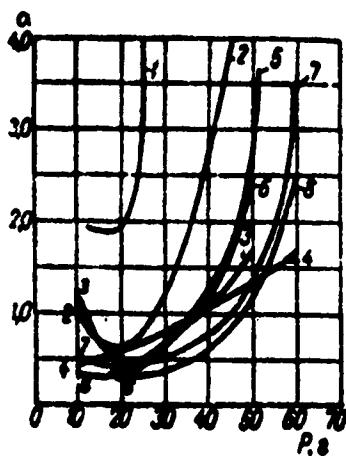
Fig.2.Relation of relative derivative α to load for
a few refractory compounds and silicon; 1...Si;
2...CbB$_2$; 3...TiN; 4...SiC; 5...ZrC; 6...TiC;
7...CrB$_2$; 8...Cr$_3$C$_2$.
(On abscissa: P, in grams).

at the comparison of the microbrittleness curves in case of a load
that corresponds to the minimum value of α,i.e.,in the given case
with a load of P = 20 g.

The analysis of the curves α = f(P) indicates that with lar-
ger loads the effect of the stress field sharply increases, and it
is different for different materials. Therefore,obviously,the com-
parative brittleness cannot be characterized by comparison of the
curves by loads at which all impressions have cracks, since these

magnitudes depend not only on the physical nature of the tested sample
but also on the stress field in which each measured grain happens to
be.

Attention is called to the fact that magnitude $\alpha$ is comparat-
ively large for pure Si, and sharply increases with the growth of the
load. Starting from the above made assumptions,as a result of this,it
can be expected that for samples of silicon of different grain sizes
the micro-brittleness curves will be different.Experience confirms
this assumption. On Fig.3,microbrittleness curves are shown for
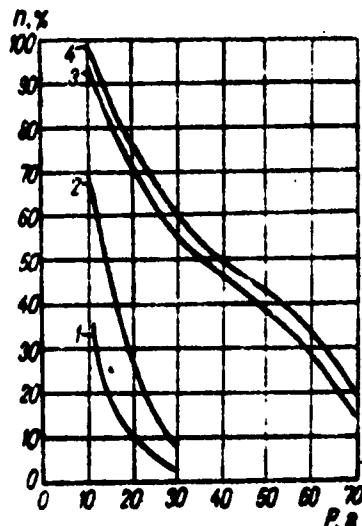


Fig.3.Curves of microbrittleness for coarse-grained and
fine-grained samples of silicon and chromium carbide:
1...silicon,sample No.1; 2...Si,sample No.2; 3...
$Cr_7C_2$ sample No.1; 4...$Cr_3C_3$ sample No.2.
(On abscissa: P,in grams)

coarse-grained and fine-grained silicon. The fine-grained samples
seem to be less brittle than the coarse-grained. This can be ex-

plained so that in the fine-grained sample the tested grain is under
conditions of a more all-round disproportionate stress than in the
coarse-grained sample, which causes the endurance of greater loads
without destruction. Generally speaking, similar conclusions can be
also drawn on the basis of the Orowan-Griffith theory.

For sake of comparison, Fig.3 also shows the microbrittleness
curves for samples of $Cr_3C_2$ of different grain size. The samples dif-
fer from each other by granularity in the same way as the Si sam-
ples. In correspondence with the considerably smaller magnitude of
$\alpha$ for $Cr_3C_2$ in contrast with Si, the difference in the micro-brit-
tleness curves for $Cr_3C_2$ is also much less. If at P = 20 g, the value
of microbrittleness for $Cr_3O_2$ differs only by 7 percent., then at
the same load it is $2\frac{1}{2}$ times larger for Si. This difference in the
curves increases with the load, together with the increase of the
value of $\alpha$, as shown in Table 1.

TABLE 1.

| Si | | | $Cr_3C_2$ | | |
|---|---|---|---|---|---|
| $P$, g | $a$ | $\dfrac{n_1}{n_{11}}$ | $P$, g | $a$ | $\dfrac{n_1}{n_{11}}$ |
| 12 | 1,9 | 1,72 | 10 | 0,3 | 1,02 |
| 20 | 1,9 | 2,50 | 20 | 0,3 | 1,07 |
| 25 | 3,0 | 3,00 | 40 | 0,6 | 1,11 |
| — | — | — | 60 | 2,2 | 1,22 |

(NOTE: P is given in grams)

Parallel with the method of construction of microbrittleness curves for qualitative comparison, we have widely used the method of electron microfractography.

The method of electron fractography ,developed by K.Zapf,i.e., the study of the structure of ruptures,lately finds larger and larger application for the investigation of the character of destruction of metals and alloys, e.g., of steel,in connection with composition,structural peculiarities,ageing,and so on,as well as for the solution of other problems of metallurgy. Deficiencies,limitations inherent in an optical microscope, -- the comparatively small magnification,the low resolving power and chiefly the small depth of sharpness -- were the motive that,in the majority of cases of steel, fractographic investigation is made with the aid of an electron microscope.

We applied the electro-micro-fractographic investigation of refractory compounds of the type of carbides,borides,nitrides and silicides in order to clarify their mechanism of destruction in connection with the study of their comparative brittleness.

Applied to fractures of refractory compounds,we worked out a special methodology of sample preparation [7] which consists of two steps. The first is the formation of an impression by pressing the tested fracture surface into aceton-softened celluloid. After drying of the impression and its separation from the surface of

the sample ,on the contact side a second impression was dusted on
with titanium or silicium protoxide (second step).The separation of
the second impression was accomplished by the dissolution of the
first in aceton.

According to this methodology,structures of brittle frac –
tures were examined for a series of multi-crystal refractory com –
pounds for which data were obtained on microbrittleness. All samples
were obtained by hot pressing of the powders of limited(maximum)com-
positions. The samples under testing were destroyed by bending im-
pact destruction.

The study of the structure of fractures discovered substanti-
al differences in the fine structure of fractures of the different
classes of compounds. We give below microphotographs of the frac-
ture structures which are most characteristic for this or that type
of compound. They were chosen from among 50 – 100 pictures observed
in the electron microscope, and they show the statistical character
of the electron microscopic observations.

A number of compounds,e.g., columbium boride $CbB_2$(Fig.4),
silicon and columbium silicide,are destroyed along a clearly formed
surface of cleavage or separation,which can be related to the low re-
sistance of detachment along this surface under the action of normal
stresses. Considering that, as a rule, under conditions of heat
shock,by the effect of thermal tensile stresses the material is de-
stroyed,owing to normal stresses,the low resistivity of these materials

Fig.5. Density of cleavage in ZrC
(x 9000)



Fig.7. Structure of fracture of TiC
(x 9000)



Fig.4.Structure of fracture of Cb
horide CbF₂, (x 9000)



Fig.6. Structure of fracture of
...-513 (x 9000)

Fig.8. Structure of fracture of chromium carbide $Cr_3C_2$
( x 500)



Fig.9. Structure of fracture of boron carbide $B_4C$ ( x 500)

against detachment along a certain crystallographic surface should be related to their negative characteristics.

In the other large group of refractory compounds, in the structure of the fracture, parallel with the surfaces of cleavage and separation, signs of destruction appear along secondary surfaces of cleavage with characteristic terrace-like structure of the fracture, reflecting the blocky structure of the crystals. In the majority of cases, in these fractures the cleavage surfaces coincide with the crystallographic surfaces of the primary cleavage, as it is seen, e.g., in zirconium carbide ZrC (Fig.5), where the surface of cleavage seems to be a surface of type (100). On Fig.6, the terrace-shaped fracture of silicon carbide is presented, and on Fig.7 that of titanium carbide.

We find the majority of carbides in this group of compounds.

Finally, in still another group of compounds, e.g., $Cr_3C_2$ and $B_4C$, new elements appear in the structure of the fractures which can be apparently related to plastic deformation in micro-volume.

From this point of view, Fig.8 is characteristic where the structure of the fracture of $Cr_3C_2$ is given. Here, two systems of bent displacement surfaces can be distinguished, including three neighboring grains. In one of the grains, two plane-slippage surfaces intersect, due to which the grain seems to be smashed at a large number of blocks somewhat disoriented with regard to each other.

Still more direct signs of somewhat increased plasticity are

the traces of dislocations (apparently,growth dislocations) whose outcrops at the boundary line appear to be in the shape of punctate chains in the structure of the fracture of boron carbide $B_4C$ (Fig.9) and chromium carbide $Cr_3O_2$. In these materials, higher resistivity to thermal shock as well as a known capacity of deformation at high- er temperatures can be foreseen when even in these materials of very great strength of interatomic bond the dislocation acquires the abil- ity to shift.

<center>Conclusions</center>

The qualitative(construction of microbrittleness curves) and the quantitative(microfractographic) investigations of brittleness of refractory metalloid compounds make possible to draw a few prelim- inary conclusions.

1. The statistical curves of microbrittleness distinctly il- lustrate the difference in the microbrittleness of the different com- pounds.

Considering the most appropriate comparison of micro-plasti- city indices at a load of 20g, the following series of the examined compounds can be recorded according to decreasing brittleness:

$Si - TiN - CbB_2 - SiC - ZrC - CrB_2 - Cr_3C_2 - TiC$.
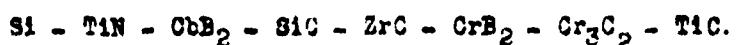
2. The obtained series is basically reproduced at taking the plasticity of "viscosity", determined by Palmquist [3],as a criter- ion. In Table 3,we give the data obtained for some compounds by Palmquist's method and by the method of constructing curves of microbrittleness.

<center>75</center>

TABLE 2.

| 1 Фаза | 2 $H$, кг/мм | 3 $P_k$, г | 4 $S \cdot 10^4$, г см | 5 $n$, % (20 г) |
|---|---|---|---|---|
| $Cr_3C_2$ | 1300 | 40 | 14,00 | 71 |
| $CrB_2$ | 1785 | 34 | 9,12 | 68 |
| TiC | 3000 | 37 | 8,26 | 73 |
| ZrC | 2925 | 26 | 4,58 | 57 |
| SiC | 3000 | 18 | 2,80 | 45 |
| $NbB_2$ | 2696 | 12 | 1,64 | 35 |

(Column headings: 1...phase; 2...$H$, kg/mm; 3...$P_k$,g;
4...$S.10^4$ g cm; 5 ...$n$,% (20g).

As it can be seen from the Table, the qualitative coincidence
of the results obtained by both methods(with exclusion of TiC) is
rather fair.

3. Investigation of the different refractory compounds of the
titanium basis(carbide,boride,nitride,and silicide) shows that the
increase in brittleness runs in the order of $TiSi_2$ - TiC - $TiB_2$ -
TiN (Fig.10).This conclusion is somewhat contradictory to the data
of Samsonov and Neshpor [1] who obtained an increase in brittleness
from titanium nitride through boride to carbide. It seems to us that
such difference is explained by an imperfection of the method of
determination of the brittle properties by the compressibility of
those powders that were used by the authors [1].
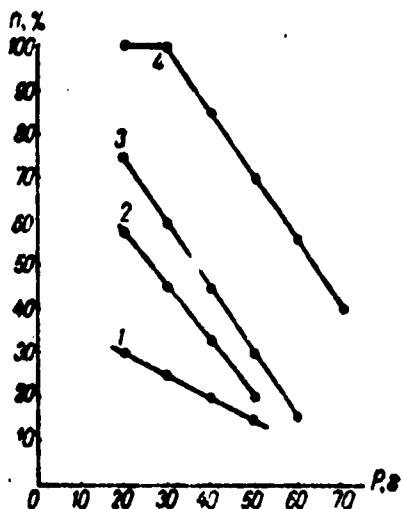
Fig.10.Curves of microbrittleness for refractory titanium
compounds: 1...TiN; 2...TiB$_2$;   3...TiC; 4...TiSi$_2$.

The theoretical explanation of this change in brittleness

from one compound to the other [1],based upon the calculation of on-

ly the force of interatomic bond does not seem to be sufficiently

strict in our presentation either,since -- parallel with the bond-

ing forces-- it is absolutely necessary to calculate the type of

bond and the different relaxation capacities. Without regard to

the fact that the value of the average square dislocation for TiC

is less(0.067) than for the boride (0.073), according to our data

TiC is more plastic,which is also qualitatively confirmed by frac-

tographic researches. This is apparently explained by the greater

metallicity of the bonding and by the greater relaxation capacity

of the carbide than of the boride. Further examinations should show
how correct such a viewpoint is.

4. Quantitative data on the comparatively large degree of mi-
crobrittleness of TiC,chromium carbide, and qualitative data correla-
ted with them and obtained by means of fractography,confirm the very
good hot -compressibility and relative high resistivity to thermal
shocks.

5. The correlative qualitative and quantitative data also co-
incide for other examined materials:— silicon,columbium boride, tita-
nium nitride,and so on.

In conclusion, the authors express thanks to G.V.Samsonov for
the samples presented for the investigation.

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## Questions and answers

Q.: What is the comparative brittleness of silicon nitride,particularly in reference to silicon carbide and other compounds?

A.N.Pilyankevich: We did not study silicon nitride.

Q.: What was the purity of the initial materials -- of boride, nitride, and so on?

A.N.Pilyankevich: They were rather pure samples,prepared from pure original materials by direct synthesis.

Q.: What was the purity of the examined silicon?

A.N.Pilyankevich: Technical silicon was examined.

Q.: What is the reproducibility of the data on microbrittleness?

A.N.Pilyankevich: We made such experiments, particularly for the chromium carbide samples obtained from a particular party. The reproducibility of the results is 5 to 10 percent. at the construction of microbrittleness curves.

# CODIFFUSION OF TWO ELEMENTS INTO HARD METAL

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In the present article the co-diffusion of two elements into a third is examined in systems of the type of ) hard metal -- mixture of two chemically active gases (. For brevity, these systems are de-signated further on as

$$Me \text{ -- } ( X' + X'' )$$

where Me...is metal(hard)

  X' ...the first element(gas)

  X''....the second element(gas).

The theoretical value of such investigations includes the ob-taining of experimental data for the explanation of the physical mech-anism of the reaction diffusion in general, practically conditioned by the need of studying the technological processes related to the action of gases upon the third phase,especially the processes of gas corro-sion and chemical thermal processing of alloys.

For the study of the structural configuration in the reaction

diffusion layers and of the kinetics of the growth of diffusion la -
yers in the triple systems of the above shown type, they must be clas-
sified.

The classification can be based upon a few factors which may af-
fect the process of reaction diffusion.

### Diagrams of the state of systems formed by compounds existing in binary systems of the Me-X type

The first case is a pseudobinary diagram of the state of com-
pounds with inorganic solubility which are formed in the Me-X' and
Me - X" binary systems. In this case, the formation of a diffusion lay-
er is observed which consists of a single phase with a concentration
gradient that for both components decreases by the layer depth. This
case is schematically presented on Fig.1 (a...for reaction diffusion;
b...for formation of triple solid solutions).
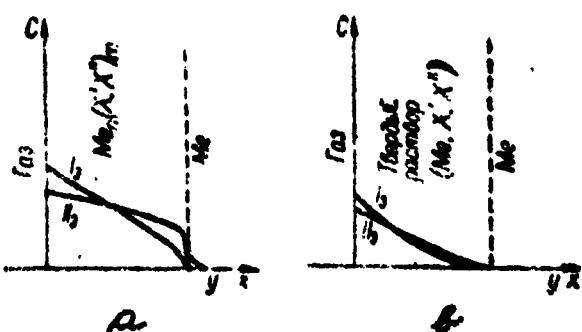


Fig.1
(Words on figure: Ordinate...gas; on "b" diagram:Solid solution)

The second case is a pseudobinary diagram of a state of X' and X" with organic solubility in compounds formed in the Me – X' and Me – X" binary systems. Here the diffusion picture already has another type (Fig.2).
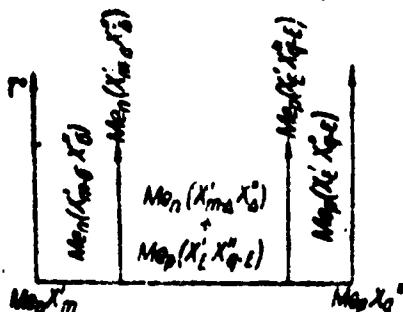


Fig.2.

The surface layer will consist of a phase which contains more of the element that has smaller diffusion mobility. At a certain depth, the layer of the other phase can also exist which has increased concentration of the element of greater diffusion mobility. This case is schematically presented on Fig.3 (a...for reaction diffusion; b... for formation of triple solid solution).

As a result of different diffusion mobilities of the elements in the reaction layers, the depth of penetration of one element will be greater than that of the other in both of the above cases.
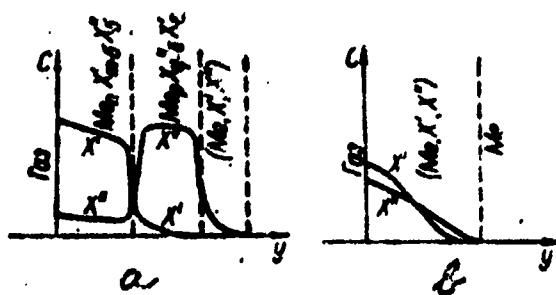
Fig.3.(No legend)
(On ordinate: Gas)

The third case is the absence of solubility of X' and X" in the binary compounds of the pseudo-binary system $Me_nX'_m$ - $Me_pX"_q$.

In this case, divergence in the chemical relationship of elements X' and X" to the metal (e.g., the chemical relationship of element X' is larger to the metal) will play the main role in the formation of the structure of diffusion layer. Here, it is supposed that under the considered conditions (at definite temperatures and pressure of the gas) both components $Me_nX'_m$ and $Me_pX"_q$ are thermodynamically stable.

On the surface of metal, a layer starts to form which consists of phases existing in the Me - X' binary system. [Note : If other compounds are present in this system beside $Me_mX'_n$, then each of them forms an independent layer; the layers are arranged one after another ]

in the order of the increase in metal content⌉ Due to the absence
of solubility of element $X''$ in it, this layer does not permit $X''$ to
penetrate into the metal, and to form a compound in the Me - $X''$ bi-
nary system. Thus, in this case there will be no interaction of the
two gaseous components with each other. If they are interacting, how-
ever, then the process can become complicated, since the metal is in
an atmosphere composed from the compound $X'_aX''_b$(which is possible,
with free excess of one of these elements). The process will limit
and regulate the interaction of the metal with the surplus element
and with the phase newly formed from the gaseous components.

### Reaction diffusion mechanism in the Me - $(X'+X'')$ system

The diffusion mechanism in the Me - $X'$ and Me -$X''$ binary sys-
tems shows influence upon the diffusion mechanism in the Me -$(X'+X'')$
system. We admit that in the Me-$X'$ binary system the metal preferab-
ly diffuses outwardly through the reaction layer, but, contrarywise,
in the Me-$X''$ binary system, element $X''$ plays the advantageous role
in the diffusion. It penetrates into the depth of the metal on whose
surface a reaction layer happens to be formed. In the triple system
Me - $(X' + X'')$ the layer arrangements are formed one after another,
correspondingly composed from phases of the $Me_nX_k$ and the $Me_pX_q$
phases( accurately speaking, $Me_nX'_{m-\delta} X''_\zeta$ and $Me_pX'_{q-\xi} X''_\xi$ ). The
character of diffusion is here qualitatively the same in each layer
as also in the corresponding binary system.

The kinetics of such processes are determined on the basis of

diffusion velocity in that of the layers of $Me_n(I'_{n-\delta} X_\delta^k)$ type

where the diffusion is the most hampered. Moreover, kinetics depends

upon the possibility of the formation of solid phases between the gas-

eous components on the metal surface. This can delay the speed of the

penetration of diffusing atoms into the metal, or the metal on the

surface prepares a scale -- a gaseous medium. This factor can also af-

fect the structural formation, since the low-lying diffusion layers

will be now under other thermodynamic conditions than without this lay-

er (different partial pressure of the gaseous components above the

phase of the type $Me_n X'_m$ and $Me_p X''_q$).

The kinetics of the processes also depend upon the phase el-

ements (or upon one of them) which are able to accelerate or slow

down the diffusion process.

The data published on the discussed problem are very few, and

for the present all mentioned cases cannot be directly confirmed by

experiments.

The second of the considered cases is confirmed by investiga-

tion conducted on co-diffusion of carbon and nitrogen in chromium

$\int 1 \int$. This system is practically very interesting. It is found that

N and C participate simultaneously in the process of diffusion into

Cr. On the surface of Cr, phases of the chromium carbide type($Cr_3C_2$,

$Cr_7C_3$) are formed with changed parameters, which indicates the solu-

tion of N in these phases. Under the carbide layers, the roentgen-

ographic and metallographic examinations found the $Cr_2N$ phase. Conse-
quently,the front of N diffusion is more quickly changing place than
the carbon front, by penetrating deep into the metal and forming a
nitride phase. In publication [1],it was shown that the overweight
of samples at the codiffusion of C and N into Cr is greater than at
the saturation with C alone. This is explained in the following man-
ner. At the intrusion of N into Cr, the volume-centered Cr lattice
is transformed into the hexagonal lattice of $Cr_2N$ which in its turn,
at diffusion of carbon, is transformed into the hexagonal lattice of
$Cr_7C_3$. The transformation of the hexagonal lattice of $Cr_2N$ into the
hexagonal lattice of $Cr_7C_3$ is easier than the transformation of the
volume-centered chromium lattice into the lattice of $Cr_{23}C_6$ at the
intrusion of the carbon alone into chromium.

In case of chromium oxide in the air, N will also participate
in the process of the reaction diffusion of O into Cr [2]. On the
surface of Cr, chromium oxide $Cr_2O_3$ is formed. Under this layer, the
layer of the hexagonal chromium nitride $Cr_2N$ is found. Here also,
the front of N diffusion is transferred into the depth quicker than
that of the oxygen. The lattice parameters of chromium oxide,which
is formed at the oxidation of Cr in the air, differ from the para-
meters of pure $Cr_2O_3$. This difference indicates that N diffusion
takes place through the oxide layer into the metal,forming a nitr-
ide layer between the oxide layer and the metal.

In both examined cases,a qualitative picture can be imagined
for the distribution of the diffusing elements in the diffusion zone.
The change in the parameter of the phases which form the external
layer is insignificant. The content of the third element,solved in
this phase,is very small. But under the external layer,a nitride lay-
er is situated in both cases. In this layer more nitrogen is contain-
ed than in the top layer. As a result,the content of the third elem-
ent ( in our two examples -- the nitrogen) at a certain depth of the
diffusion zone is greater than its content in the direct neighbor-
hood to the surface(See diagram in Fig.3a).

From the published experimental data on the research of codif-
fusion of N and C into iron, it can be concluded that nitrogen accel-
erates the saturation of iron with C,and diminishes the temperature
at the beginning of the interaction of C with iron $[3]$. It was also
established that at codiffusion of C and N into iron,the diffusion
front of N is transferred into the depth quicker than the diffusion
front of C. At simultaneous saturation of iron with C and N,the sur-
face layer is depleted from nitrogen $[5]$, i.e.,the N concentration
is the greatest at some depth of the diffusion zone.

In our opinion,the here introduced experimental data directly
confirm the second case,considered in our report at the classifica-
tion of the diffusion phenomenon in triple systems of the Me-(X'+X")
type.As to the first and the third case,unfortunately,they were not
specially investigated.

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## Questions and answers

Q.: Has there been any kind of quantitative computation for the case of diffusion of two elements?

V.N.Konev: I have already said that the first stage of the study of diffusion in triple systems was the classification of the phenomenon. Quantitative computations will be the next step.

Q.: How will the codiffusion of nitrogen and carbon monoxide run in silicon at high temperatures?

V.N.Konev: It is difficult to answer this question,because we did not learn the nature of behavior of silicon in relation to gases, especially in relation to CO. It is not known what kind of medium CO is for silicon at high temperatures --carburizing? or oxidizing? If it is both carburizing and oxidizing,then a triple system is created.

The diagram of the state and the relation of each element or compound in the silicon should be known.Then,this question can be answered.

### Discussion on the report of I.N.Frantsevich,A.N.Pilyakevich, and of V.I.Arkharov and B.N.Konev

V.S.Neshpor (Inst.of Metal Ceramics and Special Alloys,AN USSR):

It seems to me that attention should be paid to the nature of the forming phase. The point is that in the metal-metalloid systems a few phases are formed with different contents of metalloid atoms. Attention should be also paid to what kind of phase, upper,lower or in-between,is formed at the diffusion of this or that metalloid into the metal,and how the second component affects the formation of this phase.

In the works of G.V.Samsonov,it was shown that at the diffusion of silicon,as a rule,an upper phase,a disilicon,i.e.,$MeSi_2$ is formed.

This is so explained that the difference between the configuration of silicon bonds is the smallest in the elementary state,and in this phase.It is true,we should say, that the discussed researches were made only with a single metalloid,and there was no second metalloid.

This question should be studied in a further later work.

I have a number of remarks on the report of I.B.Frantsevich and A.N.Pilyankevich about microbrittleness. Their data basically coincide,with this difference that according to the data of I.N.Fran-

tsevich and A.N.Pilyankevich the nitrides are less brittle than the carbides.

In my opinion,in general the evaluation of brittleness only by the tempo of the increase of destruction with the increase of load is not sufficiently accurate. The point is that the character of the appearing cracks itself depends upon the brittleness of the substance which is being examined.

In reality,if there is any kind of impression,then at exceeding the limit of strength when the material does not have sufficient ability to disperse the elastic stresses,concentration of stress will occur at the boundaries of the impression,and as a result there is destruction of the materials. Moreover,one,two or more cracks can be formed. Obviously,the character of destruction reflects the grade of brittleness of the substance. If we say that there are two substances from which one has greater capacity of dispersing the elastic tensions,and the other has less,then the probability of crack appearance will be less in the first case.

In our works on microbrittleness,we need some other factor of brittleness which it should take in account in detail, i.e.,the degrees of brittleness were evaluated not only in relation to the number of impressions,but also to their character.

We have selected the five-degree system for the evaluation of brittleness.The average degree of destruction is:

$$z = 0\, n_0 + 1\, n_1 + 2\, n_2 + \dots$$

where $n_i$ ...is the number of impressions; the subscripts indicate the character of impressions (1...one crack on the impression; 2...two cracks,and so on). We took degree 0 for absence of cracks; degree 1... for one or two cracks; degree 2...for 2-3 cracks; degree 4...for more than three cracks, and finally degree 5 ...for complete destruction of the impression.

Such a graduation of brittleness obviously characterizes the behavior of the sample in case of brittle loading. Of course,to count only the magnitude of this degree is not enough. One has also to count the tempo of its growth with the load. It is probable that the material will be more brittle the larger is the degree of destruc - tion,i.e.,the more cracks are on the impression,and the quicker this sign increases with the load. We accepted this final factor of brit- tleness:

$$\alpha = z \frac{dz}{dp}$$

where Z...is the degree of brittleness; $dz/dp$...is the tempo of in- crease in the degree of brittleness by the load.

In our experiments,the following order of brittleness was ob- tained: -- silicide, boride, nitride, carbide. Here,by comparison with the data of I.N.Frantsevich and A.N.Pilyankevich,carbide and nitride change place.

These data fully coincide with the data on brittleness which we obtained by way of estimating the packing speed of the powders of

compounds at compression.

The coincidence of the brittleness factor,determined by two completely different methodology,gives basis for the assumption that these data are the most correct. Moreover,in the carbides the directed bonds are more marked,and the rigidity of bonding is greater,the asymmetry of vibrations smaller; therefore,they should be still more brittle than the nitrides. The dispersion of stresses in the carbides is connected with greater difficulties. This corresponds to the knowledge on the bond forces and lattice rigidity.

One should agree with the remark of A.N.Pilyankevich that not only the bonding forces influence brittleness. In the dispersion of elastic and thermal stresses,in addition to the interatomic bond,the mass of atomic complex also plays a role which also determines the vibrational mobility. Both these factors are reflected in the magnitudes of the amplitudes of atomic vibrations,computed by the Debye-Valler formula.With this magnitude,namely,we also compared the brittleness indices(See V.S.Neshpor,& G.V.Samsonov,Fizika metallov i metallovedenie(Physics of metals and metallurgy),vol.4,1957,p.181; G.V. Samsonov,V.S.Neshpor,L.Khrenova, Ibid., vol.8,1959,p.623).

The mentioned vibration considers both the bonding forces and the mass of the complex,since the frequency of vibrations and the atom mass enter into the formula.

Finally, this question is still not completely clarified,since reliable estimates of the degree of brittleness are still unavailable.

<u>V.N.Konev</u>(closing remarks); A remark was made here that at-
tention should be paid to the nature of the phases which are formed at
reaction diffusion in the triple systems. We are in agreement with this.
The point is that,in compounds of a binary system of a metal with one
element, one type of bond can predominate,and in compounds of a bina-
ry system of the same metal with another element another type of bond
can predominate. At codiffusion of these elements into the metal,the in-
dicated reason can play a substantial role both in phase formation and
in the kinetics of the process of diffusion layer formation. How this
is then reflecting upon the structural formation and kinetics,it is
difficult to say now. We need experimental data on the study of reac-
tion diffusion in systems of the type of Metal-Chemically active gases
For instance,it was pointed out here that at the diffusion in the
Me-Si system G.V.Samsonov observed the formation of only a single
phase of higher molybdaenum silicide,$MoSi_2$. It should be remarked
that there are also other data (Kiffer,Nachtigal,and Fitser) on the
phases formed at the reaction diffusion in this binary system. The
mentioned authors also observed the formation of a second molybdaen-
um silicide,$Mo_3Si_2$,arranged between the disilicide and the metal in
form of a very thin layer. It seems to us that the phase detected in
the diffusion zone depends upon which stage of process the formed pha-
ses are in (has the diffusion process stabilized? or are there still
initial phases of formation?),and upon the methods which we use for
the detection of the formed phases( an intermediate layer can form

between the two others in the shape of a very thin film).

In a short communication, all factors cannot be elucidated which could have an influence upon the process of reaction diffusion(in complex systems).

The remark of V.S.Neshpor is correct as to the kind of phases that can be formed at diffusion: -- lower,or upper in reference to the metalloid.

The point is that we have to consider here the totality of factors which influence the process of phase formation. For the establishment of the general law of reaction diffusion in triple systems of the type of(Hard metal -- Two chemically active gases) we have to have a sufficient number of experimental data on the study of diffusion in concrete systems of the indicated type.

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# STRUCTURE AND PROPERTIES OF RARE-EARTH METAL BORIDES

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Borides of the rare earth metals,of scandium,yttrium,lanthanum,
and of the lanthanides,lately found application in the electronics
[1,2] where their high thermal emission characteristics are utili-
ized: -- low work function at thermal emission, stability at low pres-
sures, stability in regard to ionic bombardment,ability to work at
high field intensities. Due to the complete absence of poisoning by
the cathodes of borides of rare-earth metals in air, they can be used
in sectional systems of electronic devices.

The use of cathodes from lanthanum boride in the synchrophaso-
tron with high field intensities (up to $10^5$ V/cm) and with a working
temperature of $1650^\circ$ permits the tapping of current densities up to

70 A/cm$^2$. With the selection of a current of 40 A/cm$^2$,the service life
of such a cathode consists of about 250 hours,but with the making of
a few special technical measures,this life can be increased even to 700-
750 hours.

The boride cathodes work well as magnetron type amplifiers with a
current density of 5 A/cm$^2$ at a field voltage of 2000 V/cm and with a
working temperature of 1500° [3].

The lanthanum boride cathode at the cyclotron of the Institute
of Physics of the AN USSR has been working for many dozens of hours.
The tantalum cathode at the same cyclotron worked 12 hours.

The auto-electronic emission of the rare-earth metal borides,
and particularly of lanthanum hexaboride [4],with a cold point,under
the effect of external electric field,permits the obtaining of a cur-
rent of about 1 A,which at an about 5-6-micron diameter,corresponds to
a current density of emission exceeding 10$^6$A/cm$^3$. [5]

In connection with these advantageous and specific properties
of boride cathodes,the Institute of Metallo -Ceramics and Special Al-
loys of the AN USSR, the Chair of Physics of Solids at the Moscow
State University, and the Scientific Research Institute of Radio En-
gineering and Electronics started a wide research on the conditions of
obtaining the properties and the structure of rare-earth metal borides.

For the preparation of rare-earth metal borides the interaction
reactions of metal oxides with boron carbides,or with boron in vacu-
um were used:

$$Me_2O_3 + B_4C \longrightarrow MeB_x + CO \uparrow$$
$$Me_2O_3 + B \longrightarrow MeB_x + BO \uparrow$$
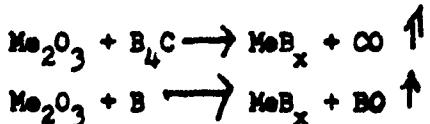
A number of new phases were detected here,among them the dibor-
ide of scandium [6],yttrium [6],lanthanum and cerium [8], praseodymium,
neodymium,samarium [9],europium [10],gadolinium [6],terbium and dys-
prosium [11,12], holmium [11,12].erbium [12],ytterbium and lutetium
[11,12]. Moreover,a number of new phases were detected,among them
the diboride of scandium [6,13], the tetraborides of gadolinium, dys-
prosium,holmium,erbium and lutetium [6,11,12,14].

## Structures and Crystallo-Chemical Peculiarities of
## Rare-Earth Metal Borides

Presently,the rare-earth metal borides of compositions $MeB_2$,
$MeB_4$ and $MeB_6$ are known.Among them the best known are the structure
and properties of the $MeB_6$ hexaborides. The first hexaborides were
described by Stackelberg and Neumann in 1932 [15] for lanthanum, ce-
rium, praseodymium, neodymium,and erbium.

The borides of composition $MeB_6$ have cubic lattice of the
type of caesium chloride,with a centered octahedron from six boron
atoms (Fig.1). It is crystallo-chemically correct when we interpret
their structure in the shape of an octahedron frame formed by B at-
oms in whose hollows the metal atoms are placed (Fig.2). The common
shape of the structure of the compounds ,and to first approximation
the size of the cell are basically determined by the frame of the B
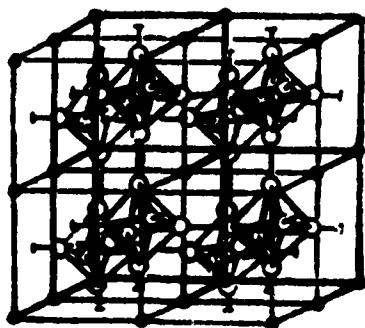
Fig.1. Structure of hexaboride; ● ...metal; o...boron.
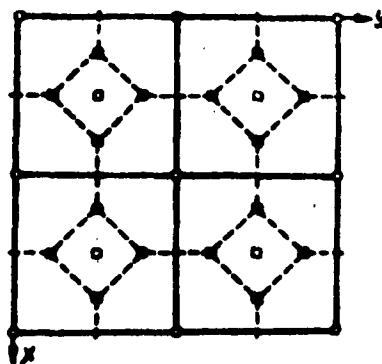


Fig.2. Projection of the structure of MeB$_6$ upon the 001 plane; o...metal; ⊓...boron; ■ boron.

atoms. The metal shows a comparatively lesser effect,although the pec-
uliarities of the cell dimension,and frequently also the properties are
related to the metal atoms. This is explained so that the hollows be-
tween the B octahedrons are rather large so that the metal atoms could
be distributed in them without strong deformation,and in some cases ev-
en with supply of free distance.

The rare-earth metal hexaborides can be divided into two sub -
groups [16] the pertinence to which is determined by the valency of
the metal atom. An analogous thought is announced in work [17] where
curves of effective atomic radii of rare-earth metals were compared
after Klemm and Bommer [18] with the lattice periods of the hexabor -
ides of these metals,and correspondence was found between the course
of the curves. While for the majority of rare-earth metals the course
of curves is characterized by a drop as the order number of metal is
growing,for europium and ytterbium an anomalous course is present,i.e.,
a sharp rise in both curves. For atomic radii this is related to a
double-plus effective valency of europium and ytterbium from whose
external shell the exit of a single electron for replenishing the def-
ect in the internal shell causes an enlargement in the size of these
atoms.

The close run of the mentioned curves indicates that the effec-
tive valency of metals in the hexaborides is near the valency in the
strictly metal crystals and,moreover,it emphasizes the metallic char-
acter of bonding in the hexaborides. On Fig.3,both curves are illus-
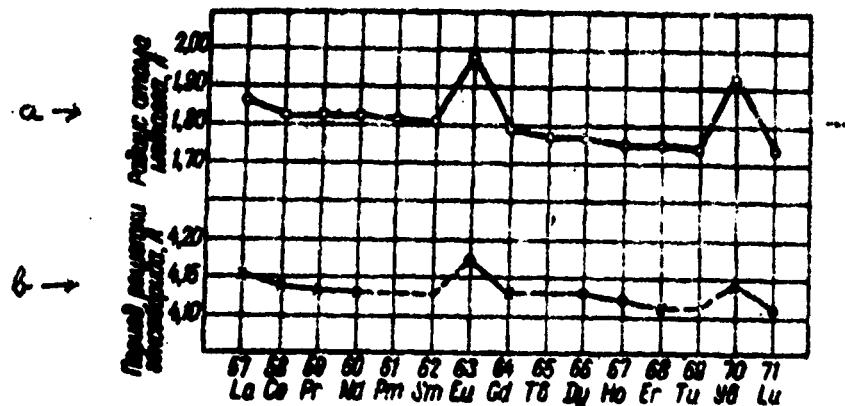
Fig.3. Relation of atomic radii of rare-earth metals /8/ and
lattice periods of their hexaborides to the order number:
●...our data; x...data of other authors.
(On ordinate: a...radius of metal atom,Å; b...lattice
period of hexaboride,Å ).

trated with computation of the data obtained by us for lattice periods

of the hexaborides of europium, holmium, dysprosium and lutetium.

In its turn,with consideration of its above indicated interpre-

tation, the character of the course of lattice period curves permits

to chose the latter values from the existing values of lattice peri-

ods GdB$_6$ a=4.112 -4.110 Å [11,19], and a=4.13 - 4.14 Å [6,20] as

well as to interpolate the approximate values of lattice periods of

the still unknown hexaborides of promethium (a $\cong$ 4.128 Å), terbium

( a $\cong$ 4.12 $\text{Å}$) and thullium (a $\cong$ 4.11 $\text{Å}$).

We tried to establish the criteria of metal hexaborides forma-
tion as follows [21]. In the $MeB_6$ borides the greatest number of mutu-
al bondings is formed between the B atoms(five),directed by the vertex
of the octahedron. The construction of these bondings cannot be real -
ized only by single electrons of the B which has the maximum valency,
equal to three. Additionally,the attraction of about two electrons
from the metal atoms is also required,which is confirmed by quantum
mechanical computations [22,23]. Due to this, the possibility of hexa-
borides formation should be related to definite magnitudes of the first
and second potentials of metal ionization characterizing the degree of
linkage of two outer electrons. By comparing the factual material on the
presence of hexaborides in metals with the ionization potentials of the
latter,we conclude that the metals can form hexaborides in the case if
the magnitude of their first ionization potential does not exceed 6.6-
-6.8 eV,and that of the second --- 11.5 to 12 eV. All rare-earth met-
als satisfy this condition, also such bivalent metals as Ca,Sr,and Ba
which,as well known, also form metalloid hexaborides.

On the basis of the data known from the literature and obtained
by us on the values of lattice periods of hexaborides,the lengths of
the Me-Me,Me-B and B-B bonds were computed. The value of the parameter
of the B atom was accepted equal to 0.207,in analogy to the structure
of $CaB_6$. The obtained lengths of bonds are given in Table 1. The ra-
tio of the bond length to the sum of atomic radii ($\alpha$) can serve as

$$\bullet - a_1 = \frac{2r_{Me}}{Me - Me}\; ; \quad \bigcirc - a_2 = \frac{r_{Me} + r_B}{Me - B}\; ;$$

$$\square - a_3 = \frac{2r_B}{B - B}.$$
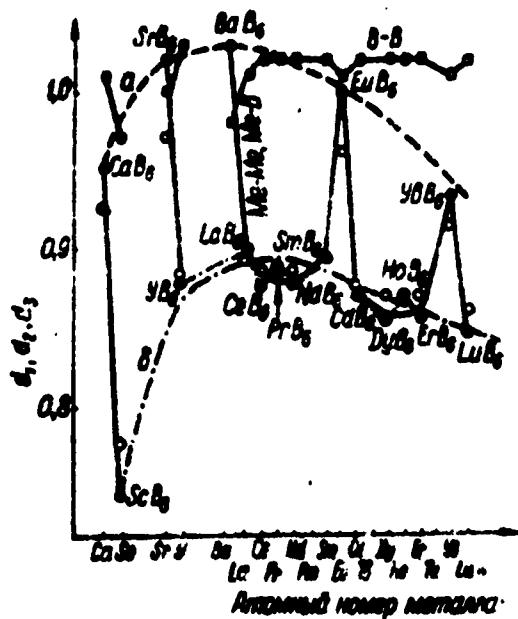
Fig.4.Relationship of values of the lines of bond lengths in hexaborides to the order of number of lanthanides.(On abscissa: Atomic number of metal)

relative characteristic of the bond's strength.

From the examination of the relationship of these ratios for Me-Me,Me-B,and B-B bonds to the atomic number of the metallic compo-

nents of the compounds,it follows that in each period the Me-Me and
Me-B linkages are diminished at the transition from bivalent into tri-
valent metals (Fig.4). In the lanthanides group,this ratio for the
Me-Me linkages gradually decreases with the increase of the metal's
atomic number. However, two sharp peaks are for the hexaborides of eu-
ropium and ytterbium in which metal ions apparently are present in
the bivalent state,similarly to the ions of Ca,Sr and Ba.

The ratio $2 r_b$ / (B-B) will change relatively little with the
change of the atomic number of the metallic components in hexaborides,
but in hexaborides of the lanthanides group it almost remains cons-
tant,somewhat decreasing in hexaborides of europium and ytterbium,which
is related to the comparatively large atomic radii of the latter.

This shows the great rigidity of the linkages of B atoms with
each other,and it explains the stability of the $MeB_6$ lattice.

Borides of $MeB_2$ composition, found for scandium and yttrium
[6,13.24], typical for the transition metals with closed d-electron
state,have a structure represented by successive alternation of hexa-
gonal layers of metal atoms, arranged in the nodes(points) of the close-
ly packed hexagonal lattice with a small ratio of c/a, and layers of B
atoms forming hexagonal two-dimensional cells (Fig.5).The spatial
structure of the $MeB_2$ type can be represented as if built from trihed-
ral prisms. The B atom is surrounded by three B atoms, and six met-
al atoms. The B atoms are in the centers of the prisms,the metal atoms
at the vertices. The metal atom is in the center of hexahedral prisms

x *Атом металла*

● *Атом бора*
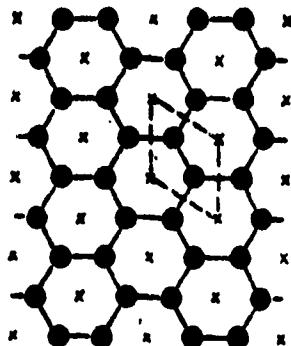
Fig.5. Structure of diboride ($MeB_2$).
(On figure: x...metal atom;
●...boron atom)

and is surrounded by 12 B atoms. The lattice period of diborides is given in Table 2.

Borides of the $MeB_4$ composition .-- According to the data in the literature, the tetraborides of uranium, thorium, cerium [17], and yttrium [24] are crystallized in the $MeB_4$ structural type. The same structural type was found by us for the tetraboride of gadolinium, holmium, dysprosium, and lutetium [11,12,14].

In Table 2, the values of the $a$ and $c$ periods (constants) of te-

- 104 -

| Фаза (1) | Me—Me, Å | $a_1 = \dfrac{2\,r_{Me}}{Me-Me}$ | Me—B, Å | $a_2 = \dfrac{r_{Me}+r_B}{Me-B}$ | B—B, Å | $a_3 = \dfrac{2\,r_B}{B-B}$ |
|---|---|---|---|---|---|---|
| CaB₆ | 4,15 | 0,952 | 3,06 | 0,925 | 1,72 | 1,01 |
| SrB₆ | 4,20 | 1,020 | 3,09 | 0,970 | 1,74 | 1,00 |
| BaB₆ | 4,29 | 1,030 | 3,16 | 0,980 | 1,78 | 0,98 |
| ScB₆ | 4,35 | 0,746 | 3,20 | 0,775 | 1,80 | 0,97 |
| YB₆ | 4,08 | 0,877 | 3,01 | 0,885 | 1,69 | 1,03 |
| LaB₆ | ,15 | 0,900 | 3,06 | 0,853 | 1,72 | 1,01 |
| CeB₆ | 4,14 | 0,877 | 3,05 | 0,885 | 1,71 | 1,02 |
| PrB₆ | 4,13 | 0,885 | 3,04 | 0,885 | 1,71 | 1,02 |
| NdB₆ | 4,13 | 0,877 | 3,04 | 0,885 | 1,71 | 1,02 |
| SmB₆ | 4,13 | 0,896 | 3,04 | 0,903 | 1,71 | 1 02 |
| EuB₆ | 4,16 | 1,000 | 3,07 | 0,961 | 1,72 | 1,01 |
| GdB₆ | 4,14 | 0,870 | 3,04 | 0,877 | 1,71 | 1,02 |
| DyB₆ | 4,13 | 0,855 | 3,04 | 0,870 | 1,71 | 1,02 |
| HoB₆ | 4,12 | 0,870 | 3,04 | 0,870 | 1,71 | 1,02 |
| ErB₆ | 4,10 | 0,855 | 3,03 | 0,870 | 1,70 | 1,02 |
| YbB₆ | 4,14 | 0,934 | 3,05 | 0,916 | 1,72 | 1,01 |
| LuB₆ | 4,11 | 0,846 | 3,03 | 0,861 | 1,70 | 1,02 |

(Note: 1...Phase)

traborides are quoted according to the different data.

The structure of tetraborides can be represented as a combination of structure $MeB_2$ and $MeB_6$ where $MeB_4$ formula itself is obtained as an arithmetic average $MeB_4 = \frac{1}{2}\,(MeB_2 + MeB_6)$. In the $MeB_4$ structure there are both trihedral prisms of the $MeB_2$ type and tetrahedral ones

TABLE 2. Lattice periods of the di- and tetra-borides of lanthanides.

| Боридная фаза | a | c | c/a | Литературный источник |
|---|---|---|---|---|
| ScB₄ | 3,140 | 3,510 | 1,118 | [14] |
| YB₂ | 3,78 | 4,40 | 1,163 | [24] |
| YB₄ | 7,01 | 4,00 | 0,573 | [17] |
| CeB₄ | 7,205 | 4,090 | 0,568 | [25] |
| PrB₄ | 7,200 | 4,11 | 0,570 | [17] |
| SmB₄ | 7,12 | 4,07 | 0,572 | [17] |
| GdB₄ | 7,13 | 3,86 | 0,541 | [6] |
| GdB₄ | 7,079 | 4,030 | 0,569 | [14] |
| DyB₄ | 7,23 | 4,09 | 0,564 | [11, 12] |
| HoB₄ | 7,15 | 4,09 | 0,572 | [11, 12] |
| HoB₄ | 7,050 | 3,992 | 0,568 | [14] |
| LuB₄ | 7,15 | 4,04 | 0,562 | [11, 12] |
| LuB₄ | 6,983 | 3,930 | 0,567 | [14] |

(Note: 1...boride phase; 2...source in literature).

similar somewhat to distorted MeB$_6$ cubes ( Fig.6). In the centers of the trihedral prisms the individual B atoms are distributed, but in the channels leading through the tetrahedral prisms there are octahedrons of B atoms. The octahedrons do not have common vertices. The B atoms from the square cross sections of the octahedrons and the B atoms in the trihedral prisms form flat cells of 4-member and 7-member rings. Thus, the structural ground of MeB$_4$ appears to be a combination of MeB$_2$ and MeB$_6$.
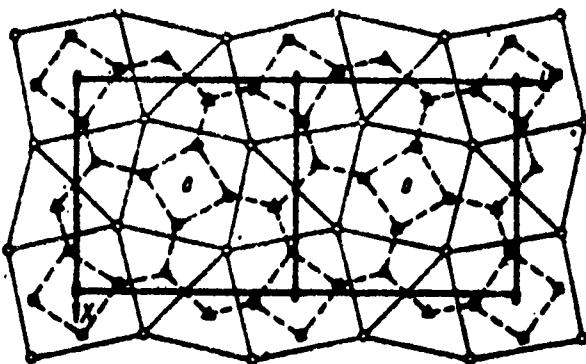
• — 4M;     0 — 4B$_I$;     ▲ — 4B$_{II}$;     ■ — 8B$_{III}$.

Fig.6. Structure of tetraborides.

## Physical properties of rare-earth metal borides

Thermionic emission.- The parameters of thermionic emission of almost all rare-earth metal hexaborides have been now investigated. On Fig.7, the relation of work function of rare-earth metal hexaborides is shown to the order number of the metallic components according to the data of [26] and supplementary data acquired by us,together with B.Tsarev and G.A.Kudintseva.

For the explanation of this relationship,the work [27] made use of the theory of atomic structure of rare-earth elements elaborated by M.A.El'yashevich [28] and of the representation of the electronic

structure of hexaborides (12,22,2.,29 - 31).

The essential content of this explanation is the following.
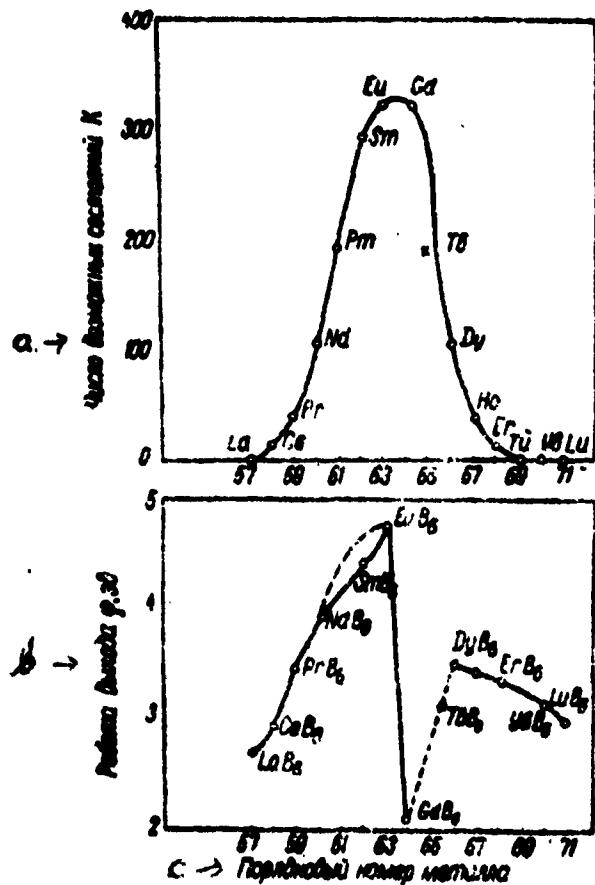


Fig.7.Relation of work function of rare-earth metal hexaborides
and of the number of possible states to the order number of
the metallic components.
(a...number of possible K states; b...work function,
$\varphi = 3b$; c...order number of metal).

The bonding between the metal and boron atoms in the hexaborides is realized by electron cooperatives formed by electrons of the normal or excited d-shell and partly of electrons pertaining to the s-shells of the metal, and not used in the linkage with boron. In the hexaborides two systems of ener  bands have to be considered -- a narrow,weakly excited 4f-band, and a comparatively wide hybrid  5d-6s band.

It is known that at the normal state the majority of the atoms in rare-earth elements do not have 5d-electrons,but on account of the vicinity of energies of the 4f and 5d states,the latter ones apparently penetrate into the hexaboride crystals,due to f-d transitions. In particular,for the doubly ionized atoms of rare-earth elements, $4f \rightarrow 4f^{n-1}$,5d transitions take place $[28]$.

The probability of f-d transitions and consequently also the degree of free conductivity electrons in the hybrid sd-band are determined by the degree of filling of the 4f-band and by the number of possible states of the f-electrons in these bands.

Since the 4-f-shell of rare-earth elements is comparatively weakly excited at the formation of chemical bond $[32]$,the maximum multiplicity of Khund(?) $[33]$ can be applied to it,according to which the larger is the stability of the shell and the degree of linkage of its filling electrons, the higher is the number of the possible terms. On Fig.7,the number of the possible terms is given for the 4f-electrons in relation to the atomic number of the metals.

The maximum multiplicity and,consequently,the greatest degree

of electron linkage and the smallest possibility of f-d transitions fits europium and gadolinium according to these data; each of them has seven electrons in the 4f-shell in the normal state.

Obviously,with the increase of linkage degree of the f-electrons and with the difficulty of the f-d transitions, the work function of the electrons ought to grow,which is qualitatively also shown by the comparison of the relation of work function and the number of possible terms To the atomic number. A sharp drop appears for gadolinium which has one 5d-electron that seems to be essentially free, similarly to the unique electron of alkaline metals. In the last rare-earth element, the lutetium,the appearance of one 5d-electron outside the closed 14-electron 4f-shell does not provoke a sharp drop in the work function at the transition from ytterbium hexaboride to lutetium hexaboride. This is due to the powerful shielding of the sd-orbits of the 4f-shell which is very much saturated with electrons in the dysprosium-lutetium series. Essentially, after its atomic structure, lutetium should be considered not a rare-earth metal but a d-transition metal, the first in the order of lutetium - platinum.

The values of work function of scandium and yttrium (correspondingly 2.96 and 2.22 eV) are subject to the laws established in work [34] for the borides of transition metals.

Thus,the hexaborides of yttrium,lanthanum,gadolinium,and lutetium which have the smallest work function have the best prospect for application in electronics.
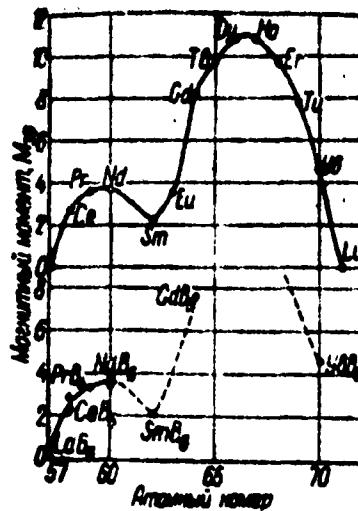
Fig.8. Magnetic momentums of the lanthanoids and of their

hexaborides.(On ordinate: Magnetic momentum,$M_3$ ; on

abscissa: Atomic number)

Magnetic properties.- On Fig.8,according to the data of the works

$\left[32,36,37\right]$ we gave the relations of the magnetic momentums of lantha-

noids and of their hexaborides To the atomic number. Both    curves

practically coincide .This fact points to a very weak participation

of the deeply situated,strongly shielded 4f-states in the organiza-

tion of bondings between the metal atoms and the complex atoms of $B_6$

in the hexaborides.

Electric and thermoelectric properties.- Information on the electric resistance of borides of lanthanides is very little at present. At room temperature, the specific resistance is 17 microhm cm for $LaB_6$; 60.6 microhm cm for $CoB_6$ [8], and 260 microhm cm for $SmB_6$ [9].

Thus, the resistance of hexaborides increases with the growth of the filling of the 4f-state, i.e., with the growth of their stability, according to the rule of Khund(?).

In connection with this, it can be expected that the resistance of europium hexaboride will be the greatest and that of the hexaborides of gadolinium, ytterbium and lutetium the smallest. The character of the resistance measurement with the temperature for the hexaborides, as it was shown on the example of lanthanum hexaboride [38], is typical for the metals.

The investigation of the thermoelectric properties of hexaborides [38] indicates that the practical absence of vacancy states in the hexaborides causes a low value of thermoelectromotive force in metal vapors.

Other physical properties.- As for the borides of the transition metals, the lanthanide hexaborides are distinguished by melting at high temperatures, hardness, moderate thermal expansion coefficient, and high thermodynamic strength.

The most fully investigated are the thermal expansion coefficients of those hexaborides which with a sufficiently good expression reveal a bond with the atomic radii of the metallic components, by being increased with the decrease of the latter [19].

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### Questions and answers

Q.:In which form are the hexaborides used -- in the form of tapes, wires, or round pellets?

G.V.Samsonov: Hexaborides for cathodes are used in the shape either of powder which,with the aid of a nitrobinder,is smeared upon the tantalum cathode, and then the cathode is processed by suitable manner, or in the shape of hot-pressed specimens. At hot-pressing,cylinders are made, then these small cylinders are processed into forms required for the cathode. This processing is done by electric erosion or plate-mechanical method as well as by ultrasound.

Can wires,pellets and tapes be made from hexaborides?-- this is difficult to answer at present,but the preparation of such sec - tions would be extremely useful and necessary. The tapes or wires of hexaboride could play an important role in electronic devices. Such a question, therefore, would lest be out to the researchers of powder rolling.

PRECISION DETERMINATION OF THE LATTICE PERIODS OF BORON CARBIDES OF

$B_{2.75}$ TO $B_{6.75}$ COMPOSITION BY MEANS OF ROENTGENOGRAMS

OBTAINED WITHIN THE RANGE OF LARGE ANGLES OF

SCATTERING    ( $\Theta \rightarrow 90°$ )

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(All-Union Scientific Research Institute of Abrasives and Polishing)

Last year in the All-Union Scientific Research Institute of Abrasives and Polishing much attention was paid to the problem of in - creasing the accuracy of the roentgen method of research, particularly at the precision determination of the crystal lattice constants of different substances,and firstly of the abrasive materials-- the silicon carbide, corundum,boron carbide. As a result of the conducted experiments,first in the national practice of roentgenography,the problem of fixation of the roentgen reflection maximums in the range of large scattering angles has been solved in an exceptionally simple manner. At present,in the ordinary Debye camera( $\phi$ 57.3 mm), roentgenogram can be obtained with setting the reflection at $\Theta$ = 88.5°, and with the Sachs camera, at $\Theta$ = 89.5°.
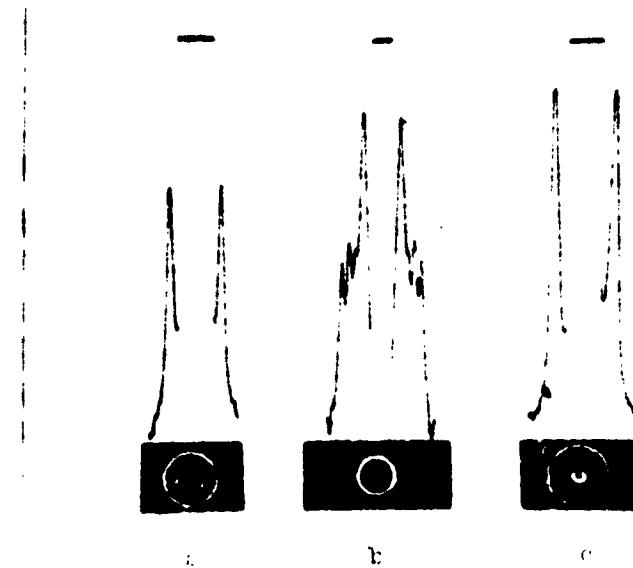
a- SiC-II:   b- P$_5$O;   c- a-A$_2$O$_5$.

Fig.1.Roentgenogram taken bythe large-angles method with
a camera having a needle collimator.

The intensity of the roentgen lines in the range of large scatter-

ing angles is rather large,and the shape of line is satisfactory which

alone permits the determination of the $\ominus$ value with very great accuracy

(Fig.1,2).

The absolute values of the lattice constants are calculated dir-

ectly by the angle $\ominus$ ,without the use of any analytical or graphical

method of extrapolation,with an accuracy in the order of $\pm$ 0.001 percent.

of the measured magnitude.
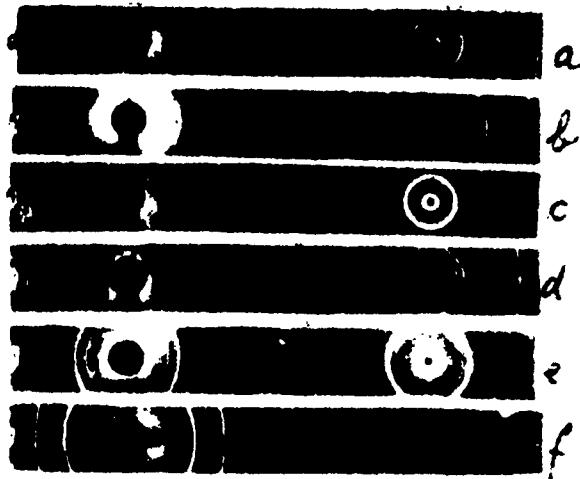
Fig.2. Roentgenogram taken by the large-angles method with a
camera having a needle collimator.
a...pyrite,alpha-radiation of cobalt; b...fluorite,alpha-
radiation of nickel; c...zirconium boride, alpha radiation of
copper; d...tantalum boride, alpha radiation of copper; e...
alpha-radiation of quartz, alpha radiation of cobalt;f...
sodium fluoride,alpha radiation of copper.

In our investigations  needle collimators were used for the ca -

mera of the Debye type (Fig.3a) and a flat cassette of new design with

needle collimator for the reverse film (Fig.3b).

The preliminary roentgen analysis of the technical samples of

boron carbide of unstable composition showed that the values of its lat-

tice periods are changed from sample to sample. In some cases, on the

roentgenograms obtained by  the large-angles  method, we observed a

Fig.3a.Roentgen Debye camera with needle collimator.
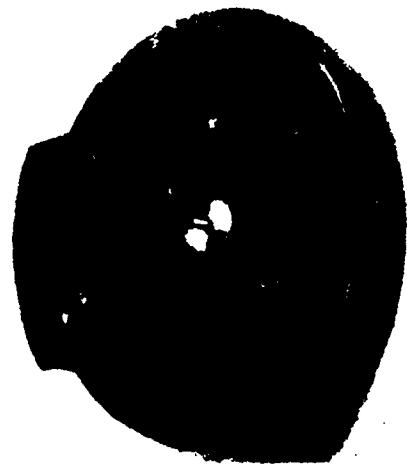


Fig.3b.Flat cassette with needle collimator for reverse
film.

very large shift of the lines, reaching $5^\circ$ (from 82 to $87^\circ$). This shift of the lines also resulted in a longer study of the lattice constants $a$ and $c$ of boron carbide. As standard, we used two boron carbide samples of the following chemical composition:

for $B_{4.45}C$:  78.68% $B_{bond}$; 19.60% $C_{bond}$; 0.20% $C_{free}$; 0.75% $B_2O_3$;

for $B_{6.75}C$:  82.86% $B_{bond}$; 13.62% $C_{bond}$; 0.33% $B_2O_3$.

These samples were subjected to multiple roentgen examinations in copper, cobalt, nickel and chromium radiation.

In the flat-cassette camera, the distance between sample and film was standardized by silver, photographed in nickel rays (hkl = 422) ($\Theta$ = $83^\circ43'$). (Fig.4). Lattice constant $a$ for silver, according to [2] was equal to 4.07724 kX.

The photography in the cylindric camera with asymmetric charge of film made it possible to determine the effective radius of the camera for each roentgenogram with great precision.

The obtained roentgenograms were photometered on a recording MPH-4 microphotometer. The microphotograms were measured on an IZA-2 comparator. The accuracy of the Debye ring camera was $\pm$ 0.05 mm.

The precision determination of the lattice periods of boron carbide was made by roentgenograms obtained in the range of large-angle scattering. For instance, at the photograph of boron carbide ($B_{4.45}C$) in copper rays, the reflections on the roentgenograms was fixed at $\Theta_{max}$ = $85^\circ57'$, and in chromium rays at $\Theta_{max}$ = $84^\circ54'$.
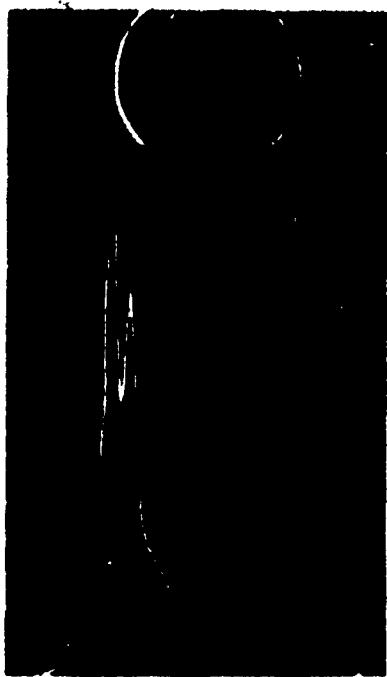
Fig.4.Roentgenogram of silver obtained at reverse
reflection in nickel rays.

The hkl indices of the reflection plane have the following values:

      344 for copper $\alpha_1$ radiation,
      328 for cobalt "    "
      419 for nickel "    "
      226 for chromium  "  "

At roentgenograms taken in cobalt rays (Fig.5) and copper rays,the

hexagonal crystal was composed of a system of two equations of quadrat-

ic form. The solution of the two-equation system gave the following
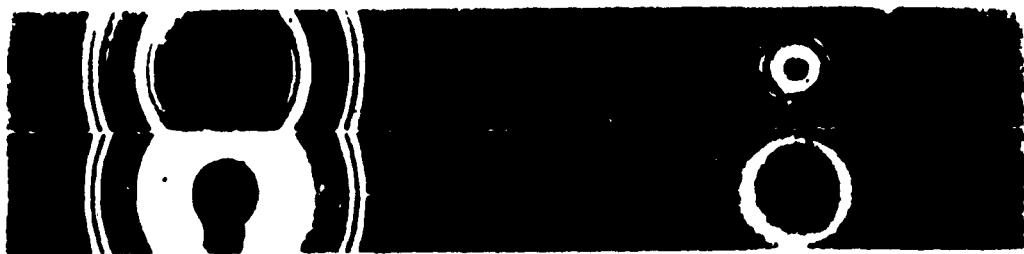
Fig.5.Roentgenogram of boron carbide $B_{4.45}C$ and $B_{6.75}C$ taken in cobalt rays with asymmetric film placement in a camera having needle collimator.

values of magnitude $a$ and $c$ for the examined samples of boron carbide:

|          | a,kX   | c,kX    | c/a   |
|----------|--------|---------|-------|
| $B_{4.45}$ C | 5.5897 | 12.0500 | 2.156 |
| $B_{6.75}$ C | 5.6300 | 12.1940 | 2.166 |

The shift of lines on the roentgenograms in the range of large-angle scattering,reaching $5^{\circ}$,seems to be the result of distortions of the crystal lattice which arise in the boron carbide as a result of the formation of a hard solid solution of boron of very high concentration.

In Table 1 we give the values of the lattice periods of boron carbide obtained by various authors.

We think that our results are very accurate and reliable since the values of lattice periods were determined by roentgenograms obtained

TABLE 1. Values of Lattice constants $\underline{a}$ and $\underline{c}$ of boron carbide

| 1 Авторы | a. кx | c. кx | c/a | hkl | θ | $B_mC$ | Излу- чение 2 |
|---|---|---|---|---|---|---|---|
| Аллен [3], 1953 г. . . . . . Жданов Г. С., Меерсон Г. А., Журавлев Н. Н., Самсонов Г. В, | 5,5967 | 12,0456 | 2,151, | 306 | 37°30' | $B_4C$ | Cu |
| [4], 1594 г. . . . . . Кудрявцев Е. И., | 5,5867 | 12,0955 | 2,165 | 603 | 76°00' 87°30' | ⟩ | Cu { Cu |
| Софронов Г. В., 1957 г. | 5,5867 | 12,0500 | 2,156 | 344 | 87°00' | $B_{4,45}C$ | Co |

(Column headings: 1...authors; 2...radiation. --
Names of authors under 1: Allen [3],1953; Zhdanov,G.S.,Meer-
son V.A.,Zhuravlev N.N., Samsonov F.B. [4],1954; Kudryavtsev
E.I.,Sofronov G.V.,1957).

in the large -angle range of scattering.

For the standard boron carbide,i.e.,the carbide with the small-
est value of $\underline{a}$ and $\underline{c}$ constants, with the proposed hkl indices and wave-
length values of the $K_a$-radiation of copper,cobalt,nickel and chromium
we calculated the possible magnitudes of ⊙ reflections (Table 2).

The experimentally observed values for boron carbide,taken in
cobalt rays,are also given.

TABLE 2. Values of the Θ angles

(Column headings : 1...hkl of reflection plane; 2...computed value, $K_{\alpha_1}$ -radiation of copper; 3...computed value, $K_{\alpha_1}$ -radiation of cobalt; 4...experimental value, $K_{\alpha_1}$ radiation of cobalt; 5...calculated value, $K_{\alpha_1}$ radiation of chromium.)

| hkl | Расчетное значение, $K_{\alpha_1}$ -излучение меди | Расчетное значение, $K_{\alpha_1}$ -излучение кобальта | Экспериментальное значение, $K_{\alpha_1}$ -излучение кобальта | Расчетное значение, $K_{\alpha_1}$ -излучение хрома |
|---|---|---|---|---|
| 011 | 9° 51′ | 11° 27,5′ | 11° 18′ | 14° 44′ |
| 003 | 11° 02′ | 12° 50,5′ | 12° 32,5′ | 16° 31,5′ |
| 102 | 11° 45′ | 13° 41′ | 13° 36′ | 17° 39′ |
| 110 | 15° 56′ | 18° 37,5′ | 18° 31′ | 24° 07,5′ |
| 014 | 17° 29,5′ | 20° 25,5′ | 20° 20′ | 26° 32′ |
| 201 | 18° 54′ | 22° 06′ | 22° 00′ | 28° 47′ |
| 113 | 19° 34,5′ | 22° 52′ | 22° 47,5′ | 29° 52′ |
| 022 | 20° 01′ | 23° 25′ | — | 30° 34,5′ |
| 105 | 20° 52,5′ | 24° 26,5′ | 24° 39′ | 31° 56,5′ |
| 006 | 22° 30′ | 26° 23,5′ | — | 34° 40,5′ |
| 204 | 24° 02,5′ | 26° 14′ | 26° 04′ | 37° 16′ |
| 131 | 25° 00′ | 29° 34′ | 29° 24,5′ | 39° 10′ |
| 212 | 26° 02,5′ | 30° 39,5′ | — | 40° 44,5′ |
| 025 | 26° 45′ | 31° 31′ | 31° 24′ | 41° 59,5′ |
| 116 | 28° 07,5′ | 33° 11′ | — | 44° 28′ |
| 017 | 28° 17,5′ | 33° 23,5′ | 33° 16′ | 44° 47′ |
| 300 | 28° 27′ | 33° 35′ | — | 45° 04,5′ |
| 124 | 29° 26,5′ | 34° 48,5′ | 34° 43′ | 46° 56′ |
| 303 | 30° 53,5′ | 36° 35,5′ | 36° 34′ | 49° 44′ |
| 215 | 31° 50′ | 37° 46,5′ | 37° 41,5′ | 51° 38′ |
| 108 | 32° 18,5′ | 38° 22′ | 38° 17,5′ | 52° 36′ |
| 207 | 33° 13,5′ | 39° 31′ | — | 54° 32′ |
| 220 | 33° 22,5′ | 39° 42′ | 39° 36,5 | 54° 50,5′ |
| 009 | 35° 02,5′ | 41° 49′ | — | 58° 34,5′ |
| 311 | 35° 10,5′ | 41° 59,5′ | 41° 54′ | 58° 54′ |
| 223 | 35° 37,0′ | 42° 33,5′ | 42° 27,5′ | 59° 57,5′ |
| 132 | 35° 55′ | 42° 56′ | 42° 50,5′ | 60° 40,5′ |
| 028 | 36° 57′ | 44° 16′ | 44° 10′ | 63° 18′ |
| 306 | 37° 40′ | 45° 12,5′ | 45° 12′ | 65° 16′ |
| 127 | 37° 49′ | 45° 24′ | — | 65° 41′ |
| 314 | 38° 49′ | 46° 42,5′ | — | 66° 41,5′ |
| 119 | 39° 32,5′ | 47° 40′ | 47° 42′ | 71° 07′ |
| 041 | 39° 40′ | 47° 50,3′ | — | 71° 36,5′ |

| hkl | Расчетное значение, $K_{a_1}$-излучение меди | Расчетное значение, $K_{a_1}$-излучение кобальта | Экспериментальное значение, $K_{a_1}$-излучение кобальта | Расчетное значение, $K_{a_1}$-излучение хрома |
|---|---|---|---|---|
| 402 | 40° 02′ | 48° 20′ | — | 72° 58′ |
| 135 | 40° 57′ | 49° 33,5′ | — | 76° 56′ |
| 01.10 | 41° 06′ | 49° 46′ | 49° 31,5′ | 77° 42,5′ |
| 218 | 41° 22′ | 50° 08,5′ | 50° 05,5′ | 79° 15,5′ |
| 226 | 42° 04,5′ | 51° 05,5′ | 51° 01′ | 84° 54′ |
| 044 | 43° 12′ | 52° 38,5′ | 52° 32′ | — |
| 231 | 44° 02′ | 53° 49,5′ | — | — |
| 322 | 44° 44′ | 54° 49′ | 54° 45′ | — |
| 405 | 45° 17,5′ | 55° 37,5′ | — | — |
| 20,10 | 45° 27′ | 55° 50,5′ | 55° 47′ | — |
| 10,11 | 46° 00,5 | 56° 40′ | — | — |
| 410 | 46° 11,5′ | 57° 40,5′ | — | — |
| 234 | 47° 32′ | 58° 56,5′ | 58° 57,0′ | — |
| 309 | 48° 15′ | 60° 02′ | 60° 03′ | — |
| 413 | 48° 48′ | 60° 54′ | — | — |
| 325 | 49° 39′ | 62° 15′ | — | — |
| 12,10 | 49° 48′ | 62° 30′ | 62° 25′ | — |
| 00,12 | 49° 57′ | 62° 44,5′ | — | — |
| 138 | 50° 05′ | 62° 57,5′ | — | — |
| 02,11 | 50° 22,5′ | 63° 26′ | — | — |
| 047 | 50° 56′ | 64° 22,5′ | — | — |
| 229 | 52° 35′ | 67° 15,5′ | — | — |
| 501 | 52° 48′ | 67° 40′ | — | — |
| 052 | 53° 32′ | 69° 02,5′ | — | — |
| 11,12 | 54° 20,5′ | 70° 39′ | — | — |
| 408 | 54° 34′ | 71° 07′ | 71° 05′ | — |
| 21,11 | 54° 52,5′ | 71° 47′ | — | — |
| 416 | 55° 18,5′ | 72° 42,5′ | — | — |
| 237 | 55° 27,5′ | 73° 02,5′ | 73° 01,5′ | — |
| 330 | 55° 36′ | 73° 22′ | 73° 22,5′ | — |
| 504 | 56° 30,5′ | 75° 34′ | — | — |
| 421 | 57° 25,5′ | 78° 07′ | 78° 07′ | — |
| 01,13 | 57° 36,5′ | 78° 40′ | 78° 40′ | — |
| 333 | 57° 53,5′ | 79° 36,5′ | 79° 36′ | — |
| 242 | 58° 12′ | 80° 44′ | 80° 43′ | — |
| 055 | 58° 50′ | 83° 31,5′ | 83° 31′ | — |
| 31,10 | 59° 00′ | 84° 30′ | 84° 36′ | — |
| 328 | 59° 18,5′ | 87° 00,5′ | 87° 03′ | — |
| 424 | 61° 25′ | — | — | — |
| 151 | 62° 25,5′ | — | — | — |
| 20,13 | 62° 37,5′ | — | — | — |
| 512 | 63° 17,5′ | — | — | — |
| 245 | 64° 00′ | — | — | — |
| 04,10 | 64° 11′ | — | — | — |
| 30,12 | 64° 22,5′ | — | — | — |
| 13,11 | 64° 54,5′ | — | — | — |
| 336 | 65° 27′ | — | — | — |
| 507 | 65° 38′ | — | — | — |

(Table 2, Cont.)

| $1$ hkl | $2$ Расчетное значение, $K_{\alpha_1}$-излучение меди | $3$ Расчетное значение, $K_{\alpha_1}$-излучение кобальта | $4$ Экспериментальное значение, $K_{\alpha_1}$-излучение кобальта | $5$ Расчетное значение, $K_{\alpha_1}$-излучение хрома |
|---|---|---|---|---|
| 154 | 66° 57,5′ | — | — | — |
| 419 | 67° 57,5′ | — | — | — |
| 12,13 | 68° 23′ | — | — | — |
| 515 | 70° 02′ | — | — | — |
| 23,10 | 70° 16,5′ | — | — | — |
| 22,12 | 70° 30′ | — | — | — |
| 058 | 70° 42,5′ | — | — | — |
| 40,11 | 71° 10,5′ | — | — | — |
| 02,14 | 71° 25′ | — | — | — |
| 600 | 72° 19,5′ | — | — | — |
| 00,15 | 73° 07′ | — | — | — |
| 341 | 75° 28′ | — | — | — |
| 603 | 76° 21,5′ | — | — | — |
| 432 | 76° 59′ | — | — | — |
| 248 | 79° 27′ | — | — | — |
| 32,11 | 80° 17′ | — | — | — |
| 21,14 | 80° 44,5′ | — | — | — |
| 157 | 82° 06′ | — | — | — |
| 520 | 82° 36′ | — | — | — |
| 11,15 | 84° 38′ | — | — | — |
| 344 | 87° 29,5′ | — | — | — |

(NOTE. The 419 plane in the $K\alpha_1$-radiation of nickel gives a reflection under an angle of = 85°87′).

From the calculated data of Table 2 these practical conclusions are drawn.

1. At the precision determination of the interplanary distances of the lattice of boron carbide, roentgenograms must be used obtained on one of the indicated anode plates. The maximum reflection angles which can be reached here are the following:

|  | hkl | Theta |
|---|---|---|
| copper anode | 344 | 87°30′ |
| cobalt anode | 328 | 87°00′ |

|  | hkl | Theta |
|---|---|---|
| nickel anode | 419 | $85°87'$ |
| chromium anode | 226 | $84°54'$ |

2. For the precision determination of the lattice constants of boron carbide, copper and cobalt plates must be used. By two obtained roentgenograms, a system of two equations of quadratic form of the hexagonal crystal is composed. The solution of this system gives the value of constants $a$ and $c$ with an accuracy of $\pm$ 0.001% of the measured magnitude.

In some cases, the reflection 055 and 328 in cobalt rays can be used. The corresponding reflection angles will be $83°31$ and $87°00$.

The calculated values of reflection angles $\vartheta$ for the normal boron carbide with the proposed hkl indices and parameters $a =$ = 5.56967 kX, and c = 12.060 kX are given in Table 2 (spatial group $D^5_{3d}$ - $R^-3m$, condition of existence of reflections in the hexagonal aspect $h - k \pm l = 3n$)

After the extreme values of the lattice periods of boron carbides of composition $B_{2.75}C$ and $B_{6.75}C$ have been determined, firstly, with the method of large angles, the precision determination of the $a$ and $c$ constants of boron carbide can be made at all intervals of the compounds from $B_{2.75}$ to $B_{6.75}$. Secondly, the limits of the solubility of B and C in boron carbide can be accurately determined. Thirdly, it can be tried to give a structural diagram of the formation of a continuous series of boron carbides of different chemical

compositions from $B_{13}C_5$ to $B_{15}C_3$ from the elementary boron carbide $B_{12}C_3$.

For this we carried out roentgen analysis of boron carbide samples whose chemical composition is presented in Table 3 (see next page).
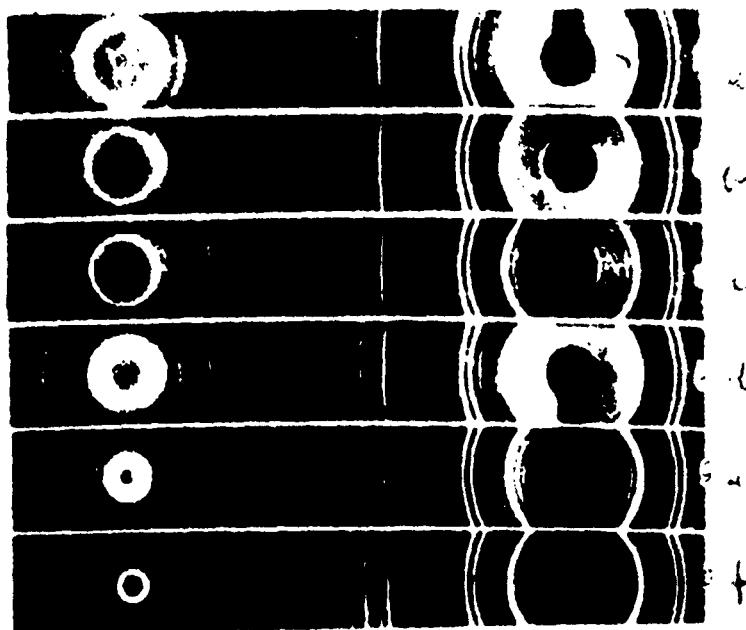


a. $n-\theta-87°00'$, B/C=2.76--4.63:
b. $b-\theta-86°32'$, B/C=4.60;
c. $c-\theta-84°41'$, B/C=5.0;
d. $r-\theta-83°15'$, B/C=5.20;
e. $c-\theta-82°47'$, B/C=5.30
f. $f-\theta-81°48'$, B/C=0.75.

Fig.6.Roentgenogram of boron carbide of different chemical composition,taken with cylindrical camera $\phi$ 68.5 mm,with needle collimator,in filtered Co rays,with asymmetric film charge.

(Addition to Fig.6,see previous page: Last plane of reflection 328 ($\textcircled{w}_{max}$).

The precision determination of the lattice periods of boron carbide,as well as the exact determination of the limits of boron and carbon solubility in boron carbide was made by the large-angles method [1]. All samples were taken twice:— in cobalt rays with the use of reflection from hkl = 328, and in chromium rays with use of reflection from hkl = 226.

For each sample,the values of $a$ and $c$ of the boron carbide lattice were determined. The results are entered in Table 3, and the roentgenograms are in Fig.6. (See preceding page).

The obtained results permit to draw the following conclusions.

1. In case of the minimum values of boron carbide, these values of lattice periods $a$ and $c$ are at the rate of $B_{bond}/C_{bond} = 2.76$ to 4.63, and the maximum values at the rate of $B_{bond}/C_{bond} = 4.75 - 6.75$.

2. The values of periods $a$ and $c$ in the $B_{2.75}C - B_{4.63}C$ interval are practically constant.

At ( a = 5.5883 - 5.5905 kX; $\Delta$ a = 0.0022 kX ; c = 12.044 - 12.055 kX; $\Delta$ c = 0.011 kX).

Periods $a$ and $c$ in interval $B_{4.75}C - B_{6.75}C$ suffer marked changes.For instance (Fig.7):

TABLE 3.(First half).Characteristics of the Boron Carbide samples $B_{2.75}C$ to $B_{0.75}C$

(Note: a...Chemical composition %; 1...$B_{bound}$; 2...$C_{bound}$; 3...$C_{free}$; 4...$Si_{bound}$; 5...$Si_{bound}$).

| | | | (a) Химический состав, % | | | | | |
|---|---|---|---|---|---|---|---|---|
| $B_{связ}$(1) | $C_{связ}$(2) | $C_{своб}$(3) | $B_2O_3$ | $Al_2O_3$ | $Fe_2O_3$ | $Si_{связ}$(4) | $Si_{своб}$(5) | Σ % |
| 69,10 | 27,78 | 0 | 0,36 | — | — | — | — | 97,25 |
| 75,00 | 24,96 | 0 | — | — | — | — | — | 99,96 |
| 87,26 | 22,00 | 9,25 | 0,92 | — | — | — | — | 99,45 |
| 61,82 | 19,56 | 11,45 | 2,14 | — | — | — | — | 97,97 |
| 66,27 | 19,73 | 7,05 | 2,63 | — | — | — | — | 96,68 |
| 72,59 | 20,15 | 1,60 | 1 72 | 1,11 | 0,46 | 0,64 | — | 96,67 |
| 69,38 | 18,33 | 2,20 | 4,15 | — | — | — | — | 94,06 |
| 73,72 | 19,34 | 2,16 | — | — | — | — | — | 96,22 |
| 70,29 | 18,27 | 3,20 | 5,40 | — | — | — | — | 97,16 |
| 72,39 | 18,70 | 2,15 | 3,36 | 0,86 | 1,22 | 0,26 | — | 96,97 |
| 78,68 | 19,60 | 0,20 | 0,75 | — | — | — | — | 99,23 |
| 71,57 | 17,48 | 0,36 | 7,42 | — | — | — | — | 96,83 |
| 63,77 | 15,27 | 1,50 | 10,86 | 0,47 | 1,15 | 0,21 | — | 93,25 |
| 73,61 | 17,12 | 0,21 | 2,02 | — | — | — | — | 93,15 |
| 77,16 | 17,49 | 1,60 | 0,78 | — | — | — | — | 97,23 |
| 74,04 | 16,20 | 0,87 | 4,23 | — | — | — | — | 96,34 |
| 76,60 | 16,52 | — | 1,90 | — | — | — | — | 96,02 |
| 77,02 | 16,53 | 0,42 | 0,55 | — | — | 0,13 | 1,27 | 96,92 |
| 7,32 | 16,21 | 0,25 | — | — | — | — | — | 93,78 |
| 82,86 | 13,62 | 0,50 | — | — | — | — | — | 96,88 |

Table 3.(Second half) Characteristics of boron carbide samples

$B_{2,75}C$ to $B_{6,75}C$

| B/C | a, кx | c, кx | c/a | $\theta_{Co-3\beta}$ |
|---|---|---|---|---|
| 2,75 | 5,5694 | 12,047 | 2,155 | 87°08' |
| 3,33 | 5,5693 | 12,055 | 2,157 | 87°00' |
| 3,39 | 5,5905 | 12,044 | 2,154 | 87°05' |
| 3,67 | 5,5697 | 12,045 | 2,155 | 87°05' |
| 3,72 | — | — | — | 87°00' |
| 3,99 | — | — | — | 87°00' |
| 4,20 | — | — | — | — |
| 4,23 | 5,5691 | 12,049 | 2,156 | 87°05' |
| 4,27 | 5,5902 | 12,046 | 2,155 | 87°04' |
| 4,29 | — | — | — | 87°00' |
| 4,45 | 5,5657 | 12,050 | 2,156 | 87°00' |
| 4,54 | — | — | — | 87°00' |
| 4,63 | 5,5694 | 12,048 | 2,155 | 87° |
| 4,78 | — | — | — | 86°30' |
| 4,89 | — | — | — | — |
| 5,07 | 5,608 | 12,148 | 2,166 | 83°32 |
| 5,13 | — | — | — | — |
| 5,17 | — | — | — | 83°15' |
| 5,29 | 5,6.6 | 12,166 | 2,166 | 82°47 |
| 6,75 | 5,630 | 12,194 | 2,166 | 81°49' |
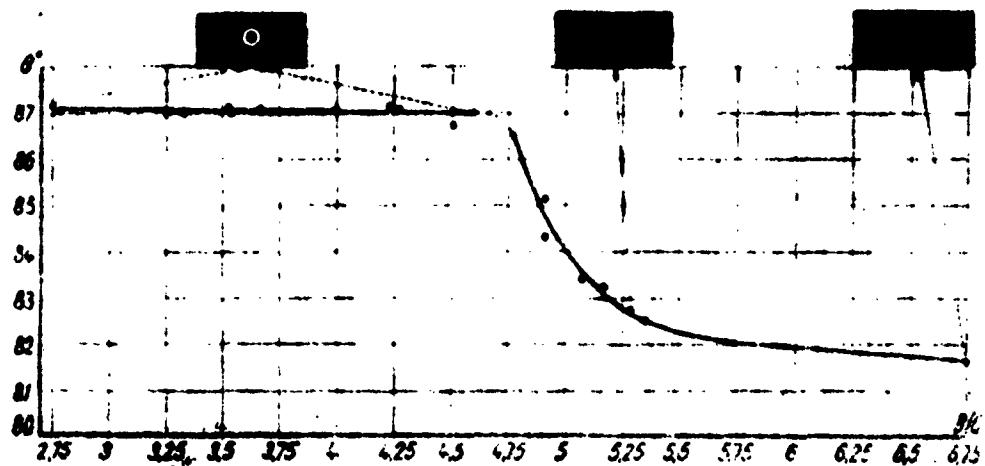
Fig.7.Relati-- of reflection angle $\Theta$ to the croportion of
boron and carbon in boron carbide,taken by the large-
angles method in cobalt rays; field of reflection hkl =
328.

We have the values

for $B_{5.07}C$      a = 5.606 kX      c = 12.148 kX

for $B_{5.29}C$      a = 5.615 kX      c = 12.166 kX

for $B_{5.75}C$      a = 5.630 kX      c = 12.194 kX

3. The boron carbides of the $B_{5.75}C$ -- $B_{4.63}C$ interval appear

as a continuous series of solid intrusion solutions of carbon or B

into the $B_{12}C_3$ lattice according to the following formula:

$$B_{12}C_{3+2} \longrightarrow B_{12}C$$
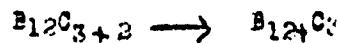
where $B_{12}O_3$ ...is the elementary boron carbide. The lattice of the $B_{12}O_3$ boron carbide is distinguished from the lattices of other compositions so that all hollows,—holes—existing in it are vacancies, i.e.,not occupied by either a B or a C atom.

According to Glaser and Moskowitz [5],the maximum number of C atoms,freely arranged in the vacancies of the ikosahedric lattice of $B_{12}O_3$ equals two, and this time $B_{12}O_3$ transits into $B_{12}O_5$. According to Clark and Hoard [6], two B atoms are freely arranged, and $B_{12}O_3$ transits into $B_{14}O_3$.

Thus,boron carbide of the composition $B_{12}O_5$ ($B_{2.4}O$) has a lattice saturated with C atoms to the maximum, and $B_{14}O_3$ ($B_{4.67}O$) is saturated with B atoms to the maximum. We consider these compositions of boron carbide critical.

4. The intrusion of additional B atoms into the lattice of the critical composition $B_{14}O_3$ may occur only by way of their replacing the central C atoms in the linear chain C • C • C. In case of complete replacement, $B_{12+2+2}O_3 = B_{15}O_2$ is formed with a linear chain C - B - C. In the $B_{14}O_3$ - $B_{15}O_2$ interval a continuous series of solid replacement solutions is formed.

The lattice periods of boron carbide are here markedly changed: -- the larger the boron concentration is in the solid solution, the larger the value of a and c is, and the smaller the angle theta is (Fig.7).

In case of boron carbide with a solid intrusion solution into the whole interval of $B_{3.75}C$ - $B_{4.63}C$, the ratio of c/a equals 3.156, and in case of boron carbide with solid replacement solution of $B_{4.63}$ - $B_{6.75}$, this ratio is increased,and it is 2.156.

According to Zhdanov,Zhuravlev, Meerson, and Samsonov /4/, the formation of a continuous series of solid replacement solutions starts earlier, i.e.,with $Be_{12}C_3$, and in case of a full substitution ,a boron carbide of the composition $B_{13}C_2$ is formed.

### Results of the investigations

1. Industrial samples of boron carbide of variable composition from $B_{2.75}C$ to $B_{6.75}C$ were investigated roentgenographically, i.e.,by the large angles method.

2. Precision determinations were conducted of the values of lattice periods of boron carbide in the $B_{2.75}C$ - $B_{6.75}C$ interval.

3. A range of continuous solid intrusion solutions or B or C was established in $B_{12}C_3$ without change in the lattice periods in the $B_{12}O_5$ - $B_{12}C_3$ - $B_{14}O_3$ intervals(See Fig.7).

4. A range of continuous series of solid replacement solutions of the central C atoms in the linear chain C - C - C was established in $B_{14}O_3$ boron.

5. It was shown that in case of full substitution,boron carbide of composition $B_{15}O_2$ is formed. The value of boron carbide periods in the $B_{14}O_3$ - $B_{15}O_2$ interval does not remain constant, but it depends upon the B concentration in the solid solution of boron

carbide.The larger the B concentration is,the larger the parameters a and c are,and the smaller is the reflection angle Theta.

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## Questions and answers

Q.: Does constant c change in the $B_{12}C_5$ - $B_{14}C_3$ interval?

V.I.Kudryavtsev: The magnitude of constant c in this interval remains without change.

Q.: What is the diameter of the needles used in the camera of needle collimator?

V.I.Kudryavtsev: For work with the Debye camera,we used a needle whose external diameter is 2 mm,and the internal diameter of the aperture is 0.4 - 0.6 mm. Needles can be also used with smaller diameter of internal aperture,but in this case the quality of the roentgenograms deteriorates.

Q.: What was the photoexposure time?

V.I.Kudryavtsev: The exposure depends upon many factors ---

on the examined material,the wave length,and so on. E.g.,for boron car-
bide photographed in cobalt rays on "Agfa" roentgen film,the maximum
exposure was 3 hours. The films were exclusively legible.

Q.: What films did you use?

V.I.Kudryavtsev: We started working with Agfa film,but later we
changed to the KF-3 film type( single-side aero-photo film) which gives
almost no background. It is true,the exposure time was increased,but
this was compensated by the clarity of the roentgenograms.

Q.: How many samples were examined and their density measured?

V.I.Kudryavtsev: The total number of examined samples reached
200. The reliability of the results can be guaranteed. The density was
determined by roentgen data from the magnitudes $a$ and $c$.

The experimental data obtained by us,expressed in the form of
a graph $\vartheta_{max} = f(B/C)$ ,made possible to precisely determine the
chemical composition of boron carbide. And they allowed the follow-
ing conclusions:

1.if the ratio is $B/C < 4.67$, then $\vartheta_{max} \simeq 87^0$(cobalt radia-
tion, hkl = 328);

2. if $B/C > 4.67$, then $\vartheta_{max} < 87^\circ$.

Reverse conclusion:

1. if $\vartheta_{max} \simeq 87^0_0$ , then $B/C < 4.67$;

2. if $\vartheta_{max} < 87^0$ , then $B/C > 4.67$.

Q: Samples of technical boron carbide contain Si. Is it pos-
sible that the ikosahedron vacancies are filled with Si atoms?

V.I.Kudryavtsev: In the Tashkent samples of boron carbide, as a rule,the Si content is    always  5 to 7 per cent.

Discussion on the report of V.I.Kudryavtsev and G.V.Sofronov

N.N.Zhuravlev (Moscow State University):

In the report of V.I.Kudryavtsev and G.V.Sofronov interesting experimental data were obtained by changing the parameters of the elementary cell of the technical samples of boron carbide with change of the content of C bound in the carbide.

The investigation of B alloys with C was done comparatively early both in our country and beyond the borders. In addition to roentgen examinations, the properties of boron carbide were also searched by different methods. The results of the measurement of the density of boron carbide samples with different content of bound C, obtained in the work of Gleiser and others, and our results of density measurements confirm to some extent the conclusion drawn in the expounded work on the formation of solid intrusion solution.

According to the data of Gleiser and others, the maximum pyknometric density in the carbon-rich boron carbide samples reaches 2.63 $g/cm^3$. In the carbon-rich samples examined by us and by G.V.Samsonov, the maximum pyknometric density was    2.60 $g/cm^3$, whereas the roentgenographic examination of the sizes of elementary cells of carbon-rich samples showed the minimum of its size.

The roentgen density,calculated from the $B_{12}O_3$( $B_4C$) composition is 2.51.$g/cm^3$.

The different experimental and roentgen densities permit to state that supplementary atoms intruded into the lattices of boron carbide of $B_{12}O_3$ composition, i.e., that solid intrusion solutions were formed.

It is interesting to compare the data of the latter investigations with the constitution diagrams suggested in the works of Samsonov and Meyerson, Samsonov, Zhuravlev, and Amnuyel' and others.

According to the data of the work of Samsonov and Meyerson, rhombohedral boron carbide is formed according to the peritectic reaction (Fig.1). This is not in agreement with the data of the works of Kudryavtsev and Gleizer and coworkers which point to the presence of a solid solution in a considerable range of concentrations.

In the work of Samsonov,Zhuravlev and Amnuyel', another possible variant of diagram was suggested for the composition of the boron-carbon system. In this case, the formation of two boron carbides of closely similar structures was suggested (work of Zhuravlev, Meyerson,Zhdanov,Samsonov). This supposition is based upon the results of roentgenographic examination of a series of boron carbide samples, rapidly cooled from high temperatures. On the roentgenograms obtained with such samples,the ends of the line splinter,i.e.,as if two types of crystal ,with closely related structures,were obtained,but with different sizes of elementary cells. These samples were related to a two-phase range.

Later, in connection with the appearance of the work of Gleiser and others, the earlier examined boron carbide samples, showing splintering of the line ends on the roentgenogram were subjected to a more delicate reduction. Then, in a heavy fluid the crystals of various densities were separated. For the separation, bromoform diluted with bensol was used. In the bromoform the crystals of maximum and minimum density separated from the sample. Roentgenographic examination showed that the boron carbide crystals, possessing both minimum and maximum densities separated from a single sample, have identical structure and are distinguished by the size of their elementary cells. Crystals with large density have smaller elementary cells than the crystals with less density.

In addition to these crystals, the samples contained particles with intermediate value of density in the range from small to large. On roentgenograms obtained from these particles, the line ends were eroded, which is explained by the presence of boron carbide crystals of different sizes of the elementary cells. Thus, the presence of boron carbide samples does not show a composition from two phases, but from crystals of different size of the elementary cells.

The results of the works of Gleiser and Kudryavtsev will harmonise with the constitutional diagram if it is assumed that on the diagram of constitution of the boron-carbon system, there is a maximum, and that boron carbide, while appearing in a phase of constant state, has a considerable area of solubility.

I.N.Frantsevich (Institute of Metal Ceramics and Special Alloys, AN USSR):

Here we witnessed the exposition of the interesting methodology of precision roentgen structural examination of structures, which in my opinion raised two questions.

Obviously, the first condition of a work with fine diaphragm is a fine-grained structure of the studied objects. E.O.Paton Institute of Electric Welding,AN USSR, gave opportunity to Mochan a few years ago to build a roentgen camera in which the same needle collimator was used as collimator. With the aid of this camera,roentgenograms of monocrystals could be taken in polycrystal objects. By the method of reverse photography,Mochan oriented the X-ray beam upon microscopic monocrystals,where the beam had a cross-section in the order of hundredths of millimeter, and he actually obtained roentgenograms for monocrystals. You probably worked with a very fine - -grained preparation, since with such fine beams you nevertheless obtained a continuous ring.

Now,as to the accuracy of determination of the parameters. Significant figures to the fourth place were given here,usually corresponding to the method of standard reverse photography. In the given case, the standard was not applied. Of course, doubt arises as to the reliability of the last significant figure introduced by You. As a rule,the method of asymmetric photography guarantees up to the third place, and not to the fourth or still less to the fifth. I

reckon that in this case it is completely unnecessary to work with standard.

V.I.Kudryavtsev : A few words in reference to the comment of I.N.Franteevich.

Our first investigations with the use of injection needles started in 1951. The experimental material what we gathered was repeatedly verified.

Due to the shortage of time, I did not say anything about the fact that at the photography of flat edges we used silver as a standard, but later,we used a more reliable standard —monocorund or thermocorund—,whose linear expansion coefficient is a few times less than for silver.

The latter comment is about boron carbide.We reckon that in the $B_{12}C_5 - B_{12}C_3 - B_{14}C_3$ interval,solid intrusion solutions of B or C atoms are formed in the boron carbide lattice without a change in the lattice constant.

In the $B_{14}C_3 - B_{15}C_2$ interval,solid solution is also formed with B replacement of the central C atoms of the C - C - C linear chain.

G.V.Samsonov (Institute of Metal Ceramics and Special Alloys,AN USSR): The data given in the report are very interesting , and they deserve attention, the more so because they mostly coincide with the data of Gleiser and coworkers and the data of Allen.

However, these data, contrary to the confirmation of V.I.Kudr-
yavtsev,do not refute at all the assumptions about boron carbide and
about the boron-carbon system earlier developed by G.A.Meerson and
myself, B.F.Ormont and coworkers and myself, N.N.Zhuravlev and I.O.
Amnuel',and so on, but in our opinion they seem to be only their fur-
ther development and supplementation (Zhurn.phys.khim.,No.8,1958).

It is a pity that at the time of the publication of the article
in the Zhurnal phys.khim., we did not know the data of V.I.Kudryav-
tsev,yet this changes practically nothing,since his data are close
to the results of Gleiser and Allen. The "compromise" forms of dia-
gram given on our work can serve as a start for further supplementa-
tion and more accurate study.

As it follows from this diagram, the lower boundary of homo-
genous region of the well freed samples of the beta-phase almost
accurately corresponds with the $B_{14}C_3$(19.2% C) composition indica-
ted by V.I.Kurdyavtsev. As to the upper boundary,this is much lower
than for $B_{12}C_5$ according to Kudryavtsev's data,although it would be
already containing 31.2 percent. C,because it goes beyond the boun-
dary of the well-established eutectics. The mechanism of the re -
placement of the C atoms in the C - C - C linear chain by B atoms
[NOTE: original has C atoms.An error ?],as indicated by Kudryavtsev
is also not new. It was worked out in the investigations of G.S.
Zhdanov and coworkers, with our participation, and previously pub-

lished in a series of communications, where only another boundary of these substitutions was indicated, corresponding to the formula $B_{6.5}C$ instead of $B_{6.75}C$ as indicated by V.I.Kudryavtsev.

The continuity of transition from the $B_{6.5}C$ phase( or, according to Kudryavtsev, from the $B_{7.65}C$) to the $B_{12}C_3$ phase( or,according to Kudryavtsev, to the $B_{12}C_5$) raises doubt since at the formation of these two phases the physical processes are not identical. Phase $B_{13}C_2$ is formed by substitution of the vacancies( the holes) with C atoms, and phase $B_{12}C_3$ — by substitution of the B atoms with C atoms.

We established this mechanism as a result of a thorough study of the physical properties of boron alloys with carbon in a wide range of carbon concentrations.

In the report,the purity of samples also raises doubt. In the majority of cases, the samples were obtained by arc fusion, which makes them strongly contaminated with silicon.

Under all circumstances,further investigations should be conducted on the properties of alloys of this important diagram,which were obtained from very pure initial components. We are now conducting such an investigation with N.F.Zhuravlev. It would be very useful if V.I.Kudryavtsev would join us. The precision method of the roentgen analysis of boron carbides which he has elaborated can find very serious application.

The first results of this work are in agreement with our pre-

vious results obtained by N.N.Zhuravlev and I.O.Amnuel'. With the ad-
dition of carbon to boron, the resistance of the latter sharply de-
creases on account of the decompensation of the bonds between the B
atoms,where the boron carbide structure is formed with a large number
of holes on place of the C atoms.

Such alloy samples possess a high conductivity of the hole
type, and high thermoelectromotor force in metal vapors( 250 - 300
microV / °C).

It should be mentioned that the expounded results are prospec-
tive in the sense of simplicity of technologically creating repro-
duceable semiconductor properties of boron alloys with carbon, and
in the sense of building upon this basis high-temperature semi-con-
ductor devices,e.g.,thermocouples resistant to high temperature,
which is the goal of research in our laboratory.

To sum up, still once more I wish to emphasize the import-
ance of the scientific research of the boron-carbon system, and I
wish to remark  on the value of the methodology and the results of
V.I.Kudryavtsev,which in themselves represent a turning point on
the road of more precise ideas about this very complicated system.

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